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Cost and Performance Report

(ER-200918)

Demonstration of the Attributes of Multi-increment Sampling and Proper Sample Processing Protocols for the Characterization of Metals on DoD Facilities

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ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
BRAC	Base Realignment and Closure
CEC	cation exchange capacity
CMIST	CRREL Multi-Increment Sampling Tool
CRREL	Cold Regions Research and Engineering Laboratory
CSM	conceptual site model
Cu	copper
DoD	U.S. Department of Defense
DQO	data quality objective
DU	decision unit
EL	Environmental Laboratory
EOD	explosive ordnance disposal
ERA	Environmental Research Associates
ERDC	Engineer Research Development Center
ESTCP	Environmental Science Technology Certification Program
FPM	FPM Group, Ltd.
FS	feasibility study
FUDS	Formerly Used Defense Sites
GPS	Global Positioning System
HPLC	high-performance liquid chromatography
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
IQR	interquartile range
ISM	Incremental Sample Methodology
ITRC	Interstate Technology Regulatory Council
LCS	laboratory control sample
MB	method blank
MMRP	Military Munitions Response Program
ND	not detected
NG	nitroglycerine
ORAP	Operational Range Assessment
Pb	lead

PCB	polychlorinated biphenyl
QA	quality assurance
QC	quality control
RI	remedial investigation
RSD	percent relative standard deviation
Sb	antimony
SI	site investigation
SU	sampling unit
SVOC	semi-volatile organic compound
TAL	target analyte list
TOC	total organic carbon
TS	Training Site
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
UXO	unexploded ordnance
VOC	volatile organic compound
Zn	zinc

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EXECUTIVE SUMMARY

BACKGROUND

Over the last decade it has been recognized that releases of energetic constituents into the environment as a result of military training occurs in an extremely heterogeneous pattern. Conventional soil sampling and sample preparation methodologies are inadequate to address the level of contaminant heterogeneity observed. Recently, there have been questions regarding whether the issues observed for the deposition of energetic constituents also substantively apply to other constituents such as metals, semi-volatile organic compounds (SVOC), and polychlorinated biphenyls (PCB).

OBJECTIVES OF THE DEMONSTRATION

This report was completed as a partial fulfillment of the obligations for ESTCP Demonstration Project ER-0918. The primary objective of this project was to develop a sampling and laboratory analysis method for metals in surface soils on military training ranges that demonstrably produces higher quality data at lower costs than conventional sampling and analysis methods.

DEMONSTRATION RESULTS

Incremental sampling methodology (ISM) including both field and laboratory protocol development was conducted at an active small arms range at Camp Ethan Allen, Vermont, as reported in *Evaluation of Sampling and Sample Preparation Modifications for Soil Containing Metal Residues* (Clausen et al., 2012b). In addition, a demonstration was conducted at three additional small arms ranges as reported in *Demonstration of Incremental Sampling Methodology for Soil Containing Metallic Residues* (Clausen et al., 2013a). The inactive ranges assessed included the 1000 inch Rifle Range at Fort Eustis, Virginia, and the Northern Area 3 of the Kimama Training Site (TS), Idaho. Both of these ranges are Military Munitions Response Program (MMRP) sites. A demonstration was also conducted at the active Range 16 Record Range located within the Small Arms Complex at Fort Wainwright, Alaska.

The demonstration followed initial protocol development at Camp Ethan Allen and included collection of 63 ISM surface soil samples and 50 conventional grab/discrete samples at Fort Wainwright; 18 ISM and 30 grab samples from Kimama TS; and 27 ISM and 33 grab samples at Fort Eustis. ISM involves both changes to the field sampling approach as well as laboratory sample preparation procedures. Each incremental sample was prepared in the field by combining a set of multiple increments (of roughly equal soil mass) that were collected over the same sampling unit (SU) using systematic random sampling.

The performance criteria used to determine whether ISM provided technically defensible data were: 1) reproducible results for surface soil samples containing metal particles, 2) improved performance of ISM as compared with conventional grab sampling techniques, and 3) ease of ISM implementability. Comparisons of ISM with the conventional grab sampling methodology demonstrated, in general, that ISM provided results more representative and reproducible for all three demonstration sites, consistent with our initial study using the results from Camp Ethan Allen.

Distributional heterogeneity was addressed by collecting at least 30–100 increments over the entire decision unit. However, multi-increment field sampling is insufficient by itself to overcome the distributional and compositional heterogeneity in the soil samples. Modifications to laboratory sample preparation procedures using United States Environmental Protection Agency (USEPA) Method 3050B are also necessary to reduce variability owing to sample heterogeneity and a proposed protocol is outlined in ISM for Metallic Residues. The proposed changes for metals adopted many of the recommendations for energetics outlined in USEPA Method 8330B such as air drying, milling, larger acid volumes to soil digestion ratios, larger digestion masses, and subsampling to build the digestate sample. Two types of milling equipment (e.g., Ball Mill and Puck Mill) yielded satisfactory results. As the digestion procedures in USEPA Method 3050B resulted in poor antimony and tungsten recoveries, alternative digestion methods were also developed for these metals.

In general, the demonstration results met the targeted performance criteria using ISM. However, there were instances where the performance criteria were not met, e.g., copper (Cu). In these situations, the results indicate the extreme contaminant heterogeneity was not adequately dealt with by the ISM approach used. Consequently, in some situations an iterative approach may be necessary whereby the ISM process is modified to meet the performance objectives, e.g., increasing the milling interval, increasing the number of increments collected, increasing the digestion mass, etc.

IMPLEMENTATION ISSUES

In addition to the published ISM for Metallic Residues protocol, the authors of this report are currently working with the USEPA to modify Method 3050B by incorporating the recommended changes identified from this project into a proposed Method 3050C. These changes include modifications to the sample preparation methods as well as the addition of an Appendix outlining the multi-increment field sampling approach, similar to what was done for USEPA Method 8330B. In the interim, *Technical and Regulatory Guidance: Incremental Sampling Methodology, ISM-1* (Interstate Technology and Regulatory Council [ITRC], 2012) is a good reference for understanding and implementing ISM. Protocols specific to ISM sampling of sites with metallic residues can be found in ISM for Metallic Residues.

There are no known limitations to the application of ISM, as the equipment used for ISM is the same as that for conventional grab sampling. Implementation costs for ISM are lower than conventional grab sampling because fewer samples are collected, prepared, and analyzed (e.g., less supplies are consumed, less time is required to survey and select sample locations, and fewer samples are labeled and shipped to the laboratory for preparation and analysis). As multiple increments need to be collected to prepare a single sample in the field, the collection time for a single incremental sample is greater than that for a single grab sample. However, as relatively large numbers of grab samples are typically needed to provide data of comparable quality as a few incremental samples, ISM does not typically increase the total sample collection time. Once the SU corners are surveyed, there is no need to survey individual sample increment locations. In contrast, each grab sample requires surveying each location. ISM samples typically have a larger mass then conventional grab samples resulting in greater per sample shipping costs and sample preparation fees. Fewer ISM samples are analyzed than grab samples. The greatest cost savings

is incurred at the laboratory preparation step owing to fewer samples requiring preparation and analysis. Again, some additional costs are incurred with the addition of the milling and subsampling step. However, the increased costs are more than offset by fewer ISM samples. Although per–sample (unit) costs are higher for ISM, the total cost of soil sampling and analysis for ISM will generally be less than that for conventional grab sampling.

Cost savings are difficult to quantify because there is no standard procedure for determining the number of soil samples needed to characterize a study area. Conventional grab sampling designs are frequently judgmental in nature, entailing subjective criteria for selecting sampling locations and number of soil samples. However, based on a review of current practices, case studies, and the results of the demonstration at the three sites, ISM can result in a cost savings of 30-60% relative to conventional grab sampling methods.

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1.0 INTRODUCTION

Since the publication of U.S. Environmental Protection Agency (USEPA) Method 8330B (USEPA, 2006) for explosives, there have been efforts to develop incremental sampling methodologies (ISM) for other analytes, particularly metals. However, there are no published procedures for the laboratory processing of incremental samples for analytes other than energetic compounds. Sample collection and laboratory processing procedures for ISM depends on the nature of the analytes of interest. The laboratory procedures of Method 8330B, which were developed specifically for explosives and propellants, generally need to be modified for other analytes. For example, the drying, sieving, and milling procedures for soil samples described in Method 8330B are inappropriate for volatile organic compounds (VOC). Depending on the types of analytes of interest, milling can bias analytical results because of analytes losses or the addition of spurious contaminants. However, because milling increases precision, the magnitude of the biases may be outweighed by larger improvements in precision.

After the release of USEPA Method 8330B, a growing concern within the U.S. Department of Defense (DoD), Federal, and state agencies, has been that similar protocols should be adopted for the characterization of metals on training ranges and at other locations. A variety of metals are used in military munitions (Clausen et al., 2012a, 2010, 2007; Clausen and Korte, 2009a, 2009b). As munitions containing metals are frequently used on Army training lands, metals deposited by rounds can accumulate in soils. Although, the deposition of metals at military ranges has only been studied on a limited basis, like explosives, metal deposition appears largely spatially heterogeneous. Anthropogenic metals are heterogeneously distributed over training ranges as particles of various sizes, shapes, and compositions. To obtain representative samples (i.e., to ensure mean contaminant concentrations in the samples will be similar to the mean concentrations in the environmental population) and obtain reproducible estimates of the mean, the sampling design and laboratory analytical method need to address compositional and distributional heterogeneity.

1.1 BACKGROUND

The development of ISM began with the realization in the mid 1990s that energetic residues were heterogeneously distributed on ranges and the current sampling methodologies did not address this issue. Early studies of energetics yielded non-reproducible and non-representative results. The result being that some sites potentially underwent remediation that was not necessary, or conversely, no remedial activities were implemented where they should have been performed. Studies conducted in the early 2000s resulted in the development of a modified sample collection and processing methodology for energetic constituents referred to as ISM.

Anthropogenic metals are also heterogeneously distributed over active training ranges as particles of various sizes, shapes, and compositions. To address the compositional and distributional heterogeneity (e.g., to obtain a representative and reproducible estimate of the mean concentration), the sampling strategy must acquire an adequate number of particles of the constituents of interest and these particles must be present in the sample in roughly the sample proportion as the decision unit (DU). The DU is an area or volume of soil of interest (i.e., an environmental population) for which one plans to make some decision based on the outcome of the sample data. Unless stated otherwise, each DU refers to a single SU, an area (or volume) of

soil over which a set of grab samples or incremental samples have been randomly collected. In general, a DU can consist of multiple SUs, where each SU is characterized or represented by a set of n grab or incremental samples, where n denotes the "sample size" (i.e., the number of independent grab or incremental samples collected from the SU).

The ISM approach is not limited to laboratory sample processing; it also includes field sampling procedures and project planning (Table 1).

Table 1. ISM for metallic residues.

<table>
<tr><th>Project Stage</th><th colspan="3">Specific Activity</th></tr>
<tr><td rowspan="6">Project Planning</td><td colspan="3">Development of Conceptual Site Model (CSM)</td></tr>
<tr><td colspan="3">Determination of Investigation Objectives</td></tr>
<tr><td colspan="3">Identification of Data Needs</td></tr>
<tr><td colspan="3">DU Identification</td></tr>
<tr><td colspan="3">Determination of Sample Depth Interval</td></tr>
<tr><td colspan="3">Number of Increments per Sample</td></tr>
<tr><td rowspan="3">Field Implementation</td><td colspan="3">Sample Tool Selection</td></tr>
<tr><td colspan="3">DU Delineation</td></tr>
<tr><td colspan="3">Collection of Soil Sample</td></tr>
<tr><td rowspan="8">Sample Processing</td><td colspan="3">Air Drying</td></tr>
<tr><td colspan="3">Sieving</td></tr>
<tr><td colspan="3">Particle Size Reduction (Milling)</td></tr>
<tr><td colspan="2">< 2 mm (examined)</td><td rowspan="5">> 2 mm (examined and archived)</td></tr>
<tr><td colspan="2">Splitting (if necessary)</td></tr>
<tr><td colspan="2">Subsampling to Build Digestate</td></tr>
<tr><td>Metals Digestion</td><td>Energetics Extraction</td></tr>
<tr><td>Analysis</td><td>ICP-MS or ICP-OES</td><td>HPLC</td></tr>
</table>

ICP-MS – inductively coupled plasma-mass spectrometry
ICP-OES – inductively coupled plasma-optical emission spectrometry
HPLC – high-performance liquid chromatography

Well defined data quality objectives (DQO) usually need to be established during project planning to successfully implement ISM. Key elements that need to be addressed during the planning phase include: 1) CSM, 2) project objectives, 3) spatial boundaries of each DU, 4) sampling depths, 5) number of increments per sample, and 6) number of samples per DU.

To reduce the influence of compositional and distributional heterogeneity for estimating mean concentrations of energetic analytes within a DU, Method 8330B recommends collecting 30 or more evenly spaced increments to build a sample with a total sample mass of >1 kg (Clausen et al., 2013a,b; Jenkins et al., 2004a,b; 2005, 2006; Walsh, M.E. et al., 2005; Hewitt et al., 2005, 2007). The objective of this sampling technique is to obtain a representative portion of every particle size, composition and configuration (e.g., spheres or elongated particles), and to avoid over- or under-sampling any portion of the DU. This same situation applies to small arms ranges where residues of (antimony [Sb], copper, lead [Pb], zinc [Zn], etc.) are present. Instead of collecting and analyzing individual grab samples and integrating the results over an area of interest (DU), or assuming a single grab represents the entire area, samples are prepared by combining a number of soil increments collected over the entire DU to obtain sample mass of approximately 1 kg. The increments can be collected using simple random sampling or

systematic random sampling. For systematic random sampling, a random starting point is selected and evenly spaced increments are collected as the sampler walks back and forth from one corner of the DU to the opposite corner (Figure 1).

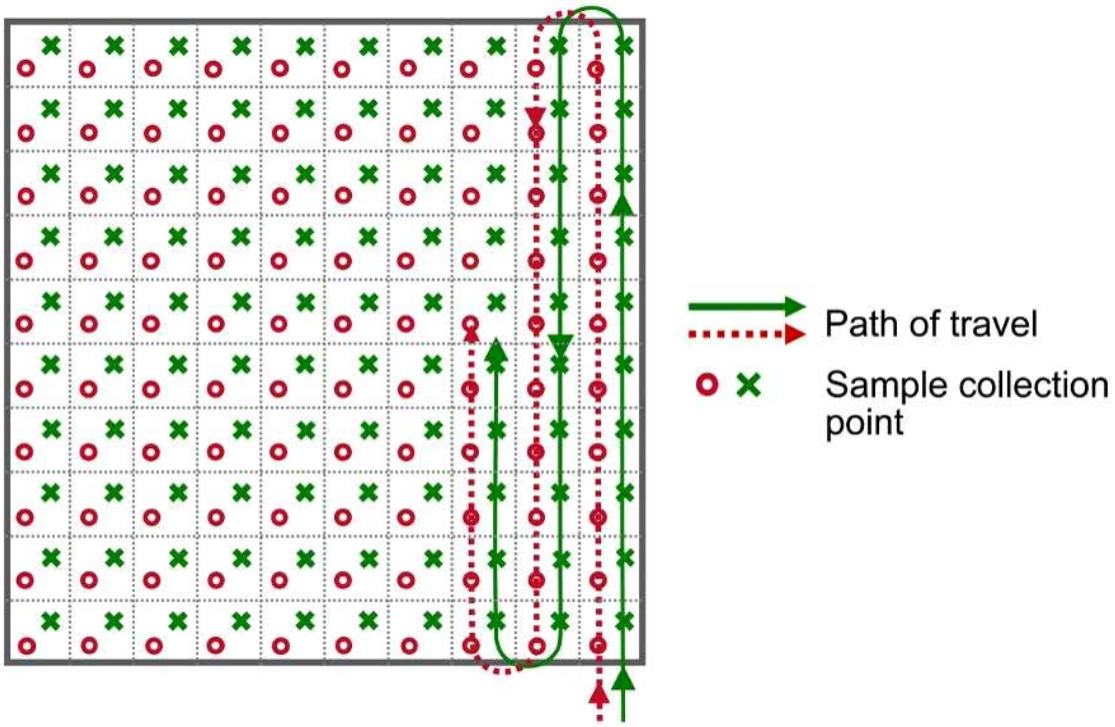

Figure 1. Example of multi-increment sampling using a systematic-random sampling design for collecting two separate 100-increment samples.

1.2 OBJECTIVE OF THE DEMONSTRATION

The primary objective was to demonstrate that the ISM approach can be readily implemented for soils with metallic residues and provides a higher quality data than conventional grab sampling and analysis methods. Specifically we wanted to demonstrate: 1) the reproducibility of results using ISM, 2) milling of soil for the analytes of interest (antimony, copper, lead, and zinc) does not introduce significant bias, 3) application of ISM yields sample results more representative of the mean soil concentration than conventional grab samples, and 4) lower total project soil sample costs. Further, we wanted to demonstrate the robustness of ISM with a variety of soil types by selecting three field sites for the demonstration. The working hypothesis is that the current field sampling approach using grab or discrete samples and sample processing procedures following USEPA Method 3050B for metals in soil does not yield representative and reproducible results for military sites where the metals are heterogeneously introduced into the environment as a solid residue. All of the objectives as discussed in Section 3.0 were met during the demonstration of ISM.

1.3 REGULATORY DRIVERS

The U.S Army's Military Munitions Response Program (MMRP) was established under the Defense Environmental Restoration Program in 2001 to manage the environmental and health and safety issues associated with unexploded ordnance (UXO), discarded military munitions, and munitions constituents on non-operational ranges in active installations, Defense Base Realignment and Closure (BRAC) sites, and Formerly Used Defense Sites (FUDS). Under the MMRP, the DoD is required to: 1) inventory non-operational ranges that contain or are suspected to contain munitions-related material released before September 2002; 2) identify, characterize, track, and report data on MMRP sites and clean-up activities; and 3) develop a process to prioritize site cleanup and estimate costs. The Army completed their inventory of non-operational ranges in 2003 and began site investigations (SI) for these MMRP sites. Based on the SI findings, some ranges may require additional assessment under the remedial investigation process. In addition, established directives mandate all active DoD facilities implement procedures to assess environmental impacts from munitions on training and testing ranges (DoD Directive 4715.11 and DoD Instruction 4715.14).

Because of the success of ISM for energetics, members of the environmental community are increasingly requiring its use for other hazardous particulate constituents such as metals (ITRC, 2012; Alaska, 2009; Hewitt et al., 2011, 2009; Hawaii, 2008). The approach is frequently used for SIs conducted under FUDS. The USEPA has issued guidance for characterization of MMRP sites using ISM (Hewitt et al., 2011) as has the U.S. Army Corps of Engineers (USACE) (USACE, 2009). Several state and federal agencies now require ISM designs. These currently include the states of Alaska, Hawaii, and the USEPA Region 6. Other states, such as Florida, are considering rewriting their environmental regulations to require ISM. Additionally, formal guidance for the states of Massachusetts, Michigan, Missouri, and New Jersey is not available but in some situations, where appropriate, ISM is being required. It is anticipated ISM will be increasingly required by additional states and USEPA regions, thus requiring DoD MMRP and Operational Range Assessments (ORAP) to employ ISM.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The technology demonstrated is the characterization of surface soil in an area of interest (DU) containing metallic residues from training with military munitions constituents using ISM. ISM entails changes to conventional field sampling methodology as well as laboratory sample preparation procedures to address the heterogeneous nature of contaminated soils. ISM also requires well-defined project DQOs during systematic planning (Table 1). The planning phase should precede any field sampling. The ITRC (2012) document provides an overview of the ISM process and Clausen et al. (2013a,b) discuss applications specific to sites with deposition of metallic residues.

In the field, the first step is to define the boundaries of the DU with markers (typically flags or stakes). The next step is to determine the approximate spacing between increments (e.g., if increments are collected using systematic random sampling) and the number of rows of increments needed to achieve the total number of increments for each ISM sample. Once the DU is identified, distributional heterogeneity is addressed by collecting a 1 to 2 kg incremental sample prepared from at least 30 to 100 increments collected randomly over the entire DU (Figure 1). The objective of this sampling technique is to obtain a representative portion of every particle size, composition (antimony, copper, lead, zinc, etc.), and configuration (e.g., spheres or elongated particles), and to avoid over- or under-sampling any portion of the DU. The increments can be collected using simple random sampling or systematic random sampling. For systematic random sampling, a random starting point is selected and evenly spaced increments are collected as the sampler walks back and forth from one corner of the DU to the opposite corner (Figure 1).

The "increments" that are combined to prepare each incremental sample typically refer to cylindrical soil cores collected using a coring device such as the "Cold Regions Research and Engineering Laboratory (CRREL) Multi-Increment Sampling Tool" (CMIST) (Walsh, 2009).

The number of replicate ISM samples required for each DU needs to be determined during project planning. The sample size will depend on the degree of variability, the tolerances for decision errors, and differences in concentrations considered significant. Typically, at least three replicates are independently collected from the DU to characterize the total variability. Additional replicates (e.g., a minimum of eight samples) will likely be needed for statistical evaluations (e.g., for two-sample hypothesis tests) when normality cannot be assumed.

If metal residues and energetics are both contaminants of interest and separate incremental samples are not collected in the field for metals and explosives, to control distributional and compositional heterogeneity, each sample must be split in the laboratory in a manner that is consistent with Pierre Gy's sampling theory and practice. Standard operating procedures to split, mill, and subsample should be developed on a project-specific basis and should be consistent with the guidance in American Society for Testing and Materials (ASTM) D6323 (ASTM, 2003) and USEPA 600/R-03/027 (Gerlach and Nocerino, 2003). As shown in Clausen et al. (2012b) successful splitting of unmilled samples with a high degree of heterogeneity usually does not occur even with a rotary splitter where many increments are collected for each split. However,

Clausen et al. (2013a,b) repeatedly demonstrated reproducible results for sample containing metal particles with splitting using a rotary splitter following drying, sieving, and milling.

Protocols for the laboratory processing of incremental samples for metals are discussed in detail in Clausen et al. (2013a,b). In general, when soils contain metal particulates (e.g., bullet fragments), the entire sample should be dried, sieved, and then mechanically pulverized. The proposed changes to the sampling processing procedures for Method 3050B are summarized in Table 2. Unfortunately, unlike for explosives, a "universal" grinder is not currently available for processing incremental samples for metals, although good success was obtained with the Puck and Roller Mills (Clausen et al. 2013a,b). The grinder needs to be selected on basis of the metals that are primarily of interest for each project. Most commercial crushing or grinding equipment possess working surfaces composed of metal alloys containing iron, chromium, tungsten (carbide), etc. These grinding surfaces have been demonstrated to introduce metal contamination during sample processing (Clausen et al., 2012b), though Felt et al. (2008) indicate the effect on soil concentrations is minimal. However, non-metallic materials are available such as an agate bowl and puck for the Puck Mill and Teflon coated cans and ceramic chips for the Roller Mill, if needed/desired.

Table 2. Salient differences between Method 3050B and proposed Method 3050C.

Activity	Method 3050B/ Conventional Sampling	Method 3050C/ Incremental Sampling Method
Field sampling	Not explicitly addressed in method. Typically, grab samples are collected with a metal scoop from biased sample locations.	An incremental sample consists of 30 -100 increments collected randomly over the entire Sampling Unit (e.g., using a systematic sampling). For cohesive surface soils, an increment typically consists of a small soil cylinder (e.g., 2 – 5 cm in length) that was collected using a 2- to 4-cm diameter coring device (e.g., as shown in Figure 2).
Sample mass and containers	Typically, about 200 g of soil in 4 oz. wide-mouth screw-top jars.	Typically, 1-2 kg of soil in clean large (e.g., 15 ×15 inches, 6 mm thick) polyethylene plastic bags sealed with Ty-wraps.
Sample drying	Sample drying is optional and not typically done.	Sample is air-dried at room temperature by spreading it onto tray to form a relative thin uniform slab.
Sieving	"…sieve, if appropriate and necessary, using a USS #10 sieve…" Soil samples are typically not sieved.	Samples are routinely passed through a #10 (2 mm) sieve. Both size fractions are weighed and < 2 mm fraction is additionally processed.
Milling	"Wet samples may be dried, crushed, and ground to reduce sample variability…" Milling is typically not done.	Samples are routinely milled using appropriate mechanical grinders, such as puck or roller mills. Milling must result in finely ground material of uniform appearance and texture.
Laboratory sub-sampling	"Mix the sample thoroughly to achieve homogeneity…" Soil is often stirred with a spatula or similar device (often in original container) and a single aliquot (e.g., scooped from the top of the container) collected as the sub-sub-sampled for digestion and analyses.	After grinding, the soil is spread onto a large tray to form a thin slab of material of uniform thickness. At least 20 small aliquots are randomly collected over the entire slab with a spatula or similar device and composited to prepare a sub-sample for digestion and analysis.
Sub-sample mass	1- 2 g wet weight or 1 g dry weight	2 - 10 g dry weight

Digestion generally follows the procedures outlined in USEPA Method 3050B with the following changes. It is recommended that more than 1 g of material be digested, preferably 5 g, maintaining a 1:1 ratio of acid to soil (Clausen et al., 2013b). Digestion masses greater than 5 g are potentially problematic due to foaming or effervescence that can overtop the 100-ml vials used with standard digestion blocks. Clausen et al. (2012b) found improved sample reproducibility and reduced sample variability with increasing mass with the differences statistically significant, although the magnitude of change was small.

The ISM discussed above is based on studies with energetics (Walsh, et al., 2009) and transitioning into metals (Clausen et al., 2012b). A chronological summary of the development of ISM is provided in Table 3.

Table 3. Chronological summary of multi-increment sampling.

Time Period	Activity	References
1960s−1990s	Recognition of the role of heterogeneity in distribution of metals in mining samples and development of methods to obtain representative samples	Duncan, 1962; Johanson, 1978 Elder et al., 1980 Gy, 1992, 1999 Wallace & Kratochvil, 1985 Pitard, 1993 Leutwyler, 1993; Studt, 1995
Early 1990s−2004	Demonstration of presence of energetic residues on ranges	Racine et al., 1992 Jenkins et al., 1997a, b, 1998, 2001 Walsh, M.E.& Collins, 1993 Walsh, M.E. et al., 1997 Thiboutot et al., 1998, 2000a, b, 2003 Ampleman et al., 2003a, b Clausen et al., 2004 Pennington et al., 2004 Taylor et al., 2004
1990s	Recognition of heterogeneity issues associated with environmental samples	Pitard, 1993 Jenkins et al., 1996
Mid 1990s−Early 2000s	Recognition of heterogeneity issues for energetic constituents on military ranges	Racine et al., 1992 Jenkins et al., 1997a, b, 1999, 2000 Taylor et al., 2004 Walsh, M.E. et al., 1993, 1997
2001−2009	Development of sampling and sample processing methods for soils containing energetic constituents	Jenkins et al., 2001, 2004a, b, 2005, 2006 Thiboutot et al., 2002 Walsh M.E. et al., 2002, 2003, 2005, 2006 Walsh M.E. & Lambert, 2006 Hewitt and Walsh, M.E., 2003 Hewitt et al., 2005, 2007, 2009
2004−2007	Demonstration and comparison of ISM with traditional grab sampling approach for soils with energetic constituents	Jenkins et al., 2004 Walsh M.E. et al., 2004 Hewitt et al., 2005 Nieman, 2007
2007−2010	Demonstration of heterogeneous distribution of metals in soils from military ranges	Clausen et al., 2007, 2010 Clausen and Korte, 2009a, b
2008−present	Adoption of ISM for soils with metals	Hawaii, 2008 Alaska, 2009 ITRC, 2012
2009−present	ESTCP ER-200918 Project	Clausen et al., 2013a, b

Although this document is specifically focused on the application of ISM at small arms ranges it has potential application to any site where solid metallic residues are introduced into the environment. At military installations this could include impact areas where artillery, mortar, or anti-tank rockets were fired because these munitions contain metals in the ordnance casing. In addition, many pyrotechnic devices contain metallic salts (Clausen et al., 2012a), so if training or maneuver areas are being sampled where these devices have been used then ISM is appropriate. The protocol outlined in Clausen et al. (2013a,b) was successfully utilized for sampling metallic residues derived from pyrotechnic training (Clausen et al., 2012a).

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantages of ISM include: 1) a soil sample representative of the area of interest, i.e., DU, 2) ability to quantify the uncertainty for field sampling and laboratory sample and analysis; and 3) reduction in the number of field samples collected for laboratory analysis (Table 4). The disadvantages of the ISM include: 1) increased volume of individual samples sent to the analytical laboratory, 2) necessity of a particles size reduction step, e.g. milling, during sample preparation, and 3) alteration of the soil matrix during the particle size reduction step possibly changing the availability of some metals during acid digestion (Table 4).

Table 4. Comparison of the advantages and disadvantages of ISM.

Activity	Advantages	Disadvantages	Comment
Total Sample Error	☑		Quantification of error possible with ISM
Number of Soil Samples	☑		Fewer samples needed with ISM
Individual Sample Mass		☑	Greater sample mass to handle heterogeneity
Precision of Result	☑		Greater sample result precision with ISM
Laboratory Preparation		☑	More involved with ISM (drying, milling, subsampling)
Field Costs	☑		Fewer samples to collect and ship with ISM
Sample Preparation Costs		☑	Higher costs due to more involved processing
Soil Matrix Alteration		☑	Possible changes to metal recovery due to milling
Milling Cross-Contamination		☑	Possible metal cross-contamination from milling when using metallic components
Metal Ratios Analysis		☑	The averaging effect of ISM is not conducive for metal ratio analysis

Processing of soil samples so they can be reproducibly sub-sampled often involves a particle size reduction step, such as milling (Clausen et al., 2013a,b). Increasing the surface area of a soil matrix may make some metals more available for acid digestion. A recent study using three soil types and three grinding techniques compared results with those obtained for samples that were blended without pulverization. Overall, the milling step increased precision and only slightly increased metal concentrations (Felt et al., 2008). One potential drawback is that samples from areas of concern (DU) and from background locations will need to be collected and processed using the same protocols. This requirement may increase the number of samples that need to be collected, processed, and analyzed, thereby increasing costs as compared to using conventional approaches. However, collection of an inadequate number of samples with conventional sampling designs often results in large data variances making reliable quantitative statistical

comparisons difficult. Background comparisons using ISM can often be done using smaller numbers of samples as the approach tends to reduce the variability and normalize distributions. It is anticipated the use of ISM will significantly increase the data quality of background samples (Clausen et al., 2013a).

The advantages of ISM include lower variability and an absence of skewed distributions (Clausen et al., 2013a,b). In contrast, large variability and positive skewed distributions are normally observed for grab samples. In addition, ISM yielded highly reproducible results, high precision, with percent relative standard deviations (RSD) for replicate samples of <30% suggesting that distributional heterogeneity was reasonably controlled. In contrast, measured RSDs for the grab samples typically yielded values >30% and, in some cases, in the hundreds of percent. The results of the demonstration study also suggested that ISM improved the accuracy of estimates of the mean; grab samples often under estimate the population mean. In general, the ISM results exhibit a higher mean concentration than grab sample results. This situation occurred in 60% of the sample results for the three demonstration sites and one experimental site for the metals of interest (Cu, Pb, Sb, and Zn). In instances where the ISM mean was less than the grab sample mean, the data exhibited greater variability than desired. It seems likely sample precision and accuracy could have been improved by taking all or some of the following steps: 1) increasing the number of increments collected from the DU, 2) increasing the sample mass collected from the DU, 3) increasing the number of subsampling increments to build the digestion aliquot, and 4) increasing the digestion mass. One of the advantages of ISM is the ability to assess the total sample error or error associated with specific steps of the ISM process allowing for the establishment of performance criteria. If the criteria are not met initially the ISM process can be altered to meet ones sample quality objectives.

One of the limitations of ISM is the necessity of collecting at minimum 30 increments from the DU, otherwise collecting fewer than 30 increments results in poorer data precision (Clausen et al., 2012b). A RSD of < 30% was generally achieved when the number of increments exceeded 30. However, fewer than 30 increments collected resulted in RSDs > 30%. Thus, for the situation studied, more than 50 increments were not necessary but clearly less than 30 were inadequate to obtain reproducible results. Additionally, owing to the large number of increments collected within a DU, ISM tends to result in better spatial coverage and therefore more representative samples than the conventional grab sampling approach. ISM is insufficient in of itself to overcome the distributional and compositional heterogeneity in the soil samples. Modifications to laboratory sample preparation procedures are also necessary to reduce variability owing to sample heterogeneity (Clausen et al., 2013a,b).

Another potential limitation is the typical Puck Mill used by commercial environmental laboratories contains metal components. Studies by Clausen et al. (2012b) indicated a potential for a significant increase in chromium, manganese, nickel, and vanadium concentrations as a result of cross-contamination from a metallic puck and bowl. However, contamination from the puck mill seems minimal for the small arms range metals antimony, copper, lead, and zinc (Clausen et al., 2013a; Felt et al., 2008). The cross-contamination issue becomes less important as the metal concentration of the sample increases resulting in greater separation from a regulatory action level. For antimony, copper, lead, and zinc the potential concentration increase from cross-contamination resulting from milling is < 5 mg/kg. This may be problematic in

situations where the expected DU soil concentration is within several mg/kg of an action level. However, cross-contamination issues can be avoided by using an agate puck and bowl, although these are more expensive than the metallic versions and process less material owing to their smaller size. Another alternative is the use of a Teflon lined roller mill with Teflon chips, which yielded acceptable results (Clausen et al., 2012b). It should be kept in mind that many of the small arms range bermed soils that were sampled often have lead levels, typically the principal metal of interest, in the 1000s to 100,000s mg/kg range but the decision limit for lead is often only 400 mg/kg.

3.0 PERFORMANCE OBJECTIVES

There were three quantitative performance objectives and one qualitative performance objective for the demonstration/validation of the technology (Table 5). The quantitative performance objectives were sample reproducibility, lack of sample bias, and cost reduction. The qualitative performance objective is ease of technology use. The effectiveness of the technology for soil sampling is predominately a function of precision of replicate laboratory sub-sample results from the same field ISM sample and the precision of replicate field ISM sample results from the same DU. ISMs effectiveness was evaluated by collecting replicate ISM soil samples from each DU and comparing against multiple grab samples collected from the same DU (Clausen et al., 2013a). Fifteen replicate ISM samples were collected at the small arms firing range berm DU at the three sites Fort Wainwright, Fort Eustis, and Kimama TS. From the same DUs, 50 grab samples were collected at Fort Wainwright, 30 from Kimama TS, and 33 from Fort Eustis. An evaluation of sample variability was performed using statistical comparisons at the 95% level of confidence. The null hypothesis is no difference between the variances of the population of grab and ISM samples. The results indicated a significant difference between variances for the two populations with lower variances evident for ISM as compared to grab samples; observations consistent with earlier findings (Clausen et al. 2013a). A secondary goal was to achieve a percent RSD of <30% for field replicates from the same DU and <15% for laboratory sub-sample replicates with ISM. This objective was met as well with ISM but not with the grab sampling approach.

Table 5. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Performance Objective Met
Quantitative Performance Objectives			
Obtain reproducible results for surface soil samples containing metal particles	Field and laboratory replicates analyzed for metals	• Demonstrate statistically significant decreases for variability (with 95% confidence) for replicate field samples and replicate laboratory sub-samples compared with replicates processed using conventional methodology. • RSD ≤30% for field replicates within same DU • RSD ≤15% for lab replicates (for concentrations > 100 mg/kg)	Yes Yes Yes
Evaluate Bias	Method blanks (MB) and laboratory control samples (LCS) processed with ISM	Concentrations < 1/10 the ISM sample concentrations. LCS recoveries should be 70% - 130% of the expected values or the manufacturer's specifications.	Yes
Compare performance of multi-increment sampling and grab sampling for metals in soils	• Samples collected using multi-increment sampling approach and grab sampling designs • Hours or cost of field sampling effort as well as cost of sample preparation and analysis	ISM sampling design results in equivalent or superior estimates of the mean with less analyses and results in a cost savings of at least 20%.	Yes
Qualitative Performance Objectives			
Implementability	Feedback from field and laboratory personnel	ISM sampling approach can be readily implemented given appropriate equipment and planning.	Yes

Positive bias (e.g., owing to milling during sample preparation) was also evaluated by processing MBs consisting of glass material (Clausen et al., 2012b). Glass samples were milled before and after a batch of soil samples were milled. A total of seven soil samples were processed in this manner. Bias was evaluated using the criteria summarized in Table 5. For the metals of interest (antimony, copper, lead, and zinc) there was no evidence of an increase in the glass blank samples between pre- and post-milled samples (Clausen et al., 2013a,b). LCSs were also processed with each sample batch to evaluate bias. Again, there was no evidence of sample bias for the analytes of interest.

The third quantitative performance objective is ISM yields a total reduction in cost of 20%. Total reduction refers to consideration of both physical collection of soil samples in the field and sample preparation back in the laboratory. This objective was evaluated by monitoring the manpower and length of time needed for: 1) field mobilization preparation, 2) DU/sample location determination and flagging, 3) surveying of sample locations/DU, 4) physical collection of samples, 5) shipping costs of samples, 6) sample preparation costs, and 7) sample analysis during the demonstration study (Clausen et al., 2013a). Sample preparation activities assessed the unmilled approach following USEPA Method 3050B and the milled approach following our modified Method 3050B approach referred to as Method 3050C. These activities were performed for both ISM and grab samples. The outcome of this cost comparison was total ISM costs are at least 20% less than the conventional grab sampling approach (Clausen et al., 2013a).

Because the number of grab samples is often determined subjectively, environmental consultants experienced with SI and remedial investigations were polled for a hypothetical small arms range berm. The consensus seems that for a 3 m high by 100 m long berm, 7 to 10 grab samples would be appropriate, although those with a statistical background/training preferred a greater number of grab samples. ISM becomes less cost effective relative to grab sampling as the number of grab samples decreases. However, precision and presumably accuracy (for estimating the DU mean) for grab sampling significantly decreases as the sample size decreases and is usually poor relative to that provided by an equal number of incremental samples. As ISM and conventional judgmental sampling designs using grab samples does not result in comparable data quality, comparisons based solely on the per unit costs of sampling and analysis does not accurately characterize the cost of ISM relative to conventional sampling.

Implementability is a qualitative performance objective that assesses feedback from field and laboratory personnel about the ease of use of ISM. Ease of use also includes availability of tools to implement the ISM and sample processing procedures. The discussions about field sampling indicate little difference between ISM and the conventional grab sampling approach, since the same field equipment is used for both (Clausen et al., 2013a). The only major difference during sample preparation in the laboratory is with milling the sample. Implementation of this step is limited in the sense that the majority of commercial environmental analytical laboratories do not have milling equipment. However, for those laboratories that have milling equipment, the ISM approach is readily implementable.

4.0 SITE DESCRIPTION

Instead of conducting the demonstration/validation at a single site, the demonstration/validation was conducted at three sites to ensure robustness of the technology. The three sites selected and discussed below are Kimama TS in Idaho, Fort Eustis in Virginia, and Fort Wainwright in Alaska. Detailed site descriptions are provided in Clausen et al. (2013a,b).

4.1 SITE LOCATION AND HISTORY

4.1.1 Kimama Training Site (TS)

The Kimama TS is located in south-central Idaho in Lincoln County, approximately 17 miles northwest of Minidoka off of Highway 24. Kimana TS was used by the Idaho Army National Guard for armored and small arms training (Figure 2). The area where the demonstration was conducted is referred to as Training Area 3, which encompasses approximately 14,322 acres (Figure 2). Training Area 3 was used for armored maneuver training from 1974 through 1993. Three small arms ranges are located in the northwest portion of Training Area 3 and were used from 1969 through 1993. The small arms range encompasses 2355 acres of Training Area 3.

Munitions used at Training Area 3 included small arms, star clusters, riot control grenades, trip flares, practice mortar fuzes, 40mm practice rifle grenades, and M69 practice hand grenades. The ordnance used on the small arms ranges included 7.62 mm, .45 caliber (cal), .22 cal, and .50 cal. The munitions constituents (lead and antimony) were detected at levels on the small arms range during a SI warranting further investigation (FPM Group, Ltd. [FPM], 2009). A remedial investigation (RI)/feasibility study (FS) project plan was prepared in October 2010 with the fieldwork anticipated to be complete by July 2011 (FPM, 2010). Additional details about the firing range are presented in Clausen et al. (2013a,b).

4.1.2 Fort Eustis

Fort Eustis is located within the geographic boundaries of Newport News, Virginia in the southeastern portion of the state. The demonstration conducted within the cantonment area of Fort Eustis occurred on the northern berm of the 1000 inch Rifle Range (Figure 3). The 1000 inch Rifle Range is a former small arms training range used between 1920 and 1941 for target practice using 0.22, 0.30, and 0.45 cal munitions. The 1000 inch Rifle Range is estimated to cover 18.5 acres. Additional details about the firing range are presented in Clausen et al. (2013a,b).

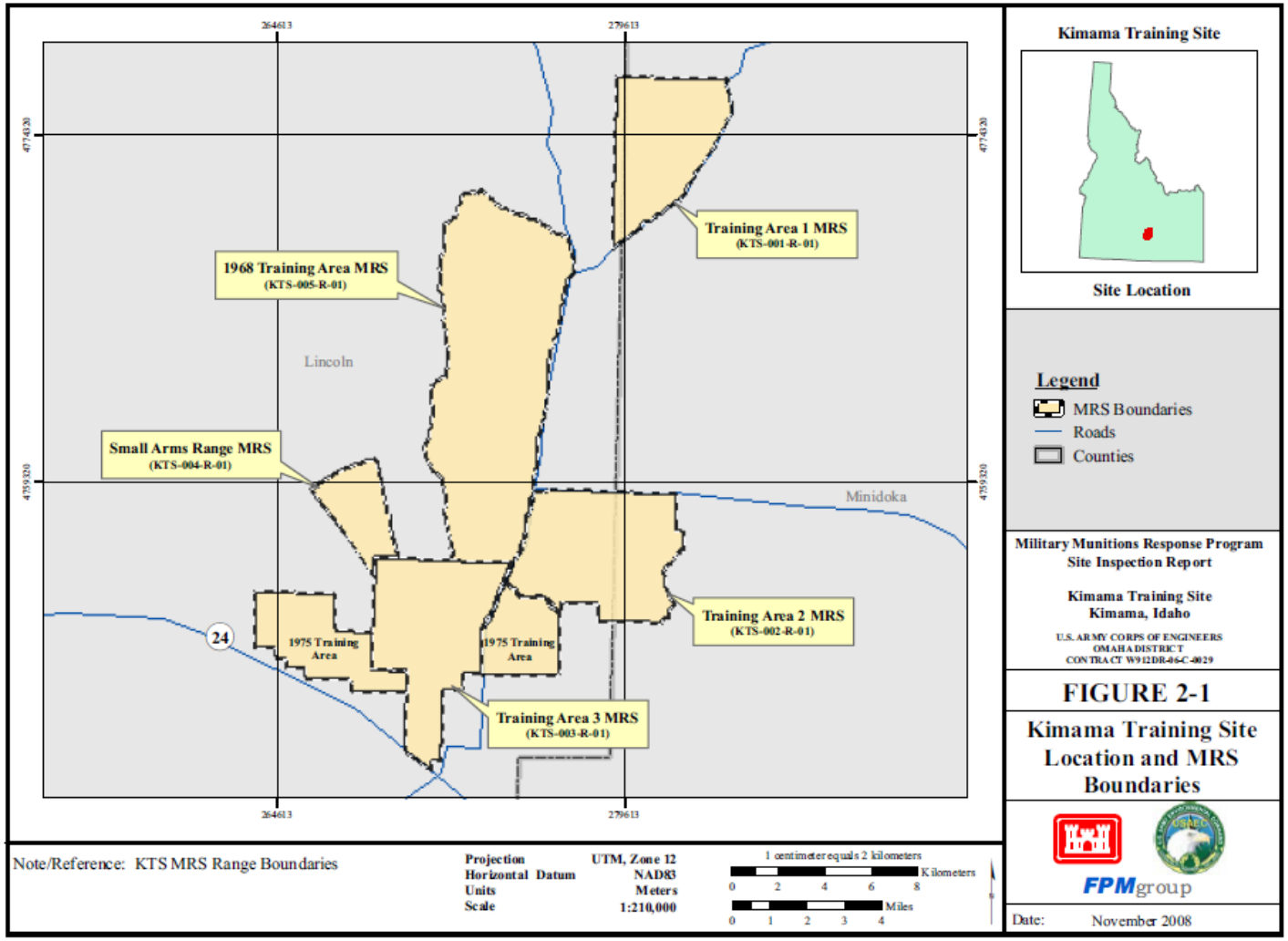

Figure 2. Location of Kimama TS, Idaho and location of Training Area 3 (FPM, 2009).

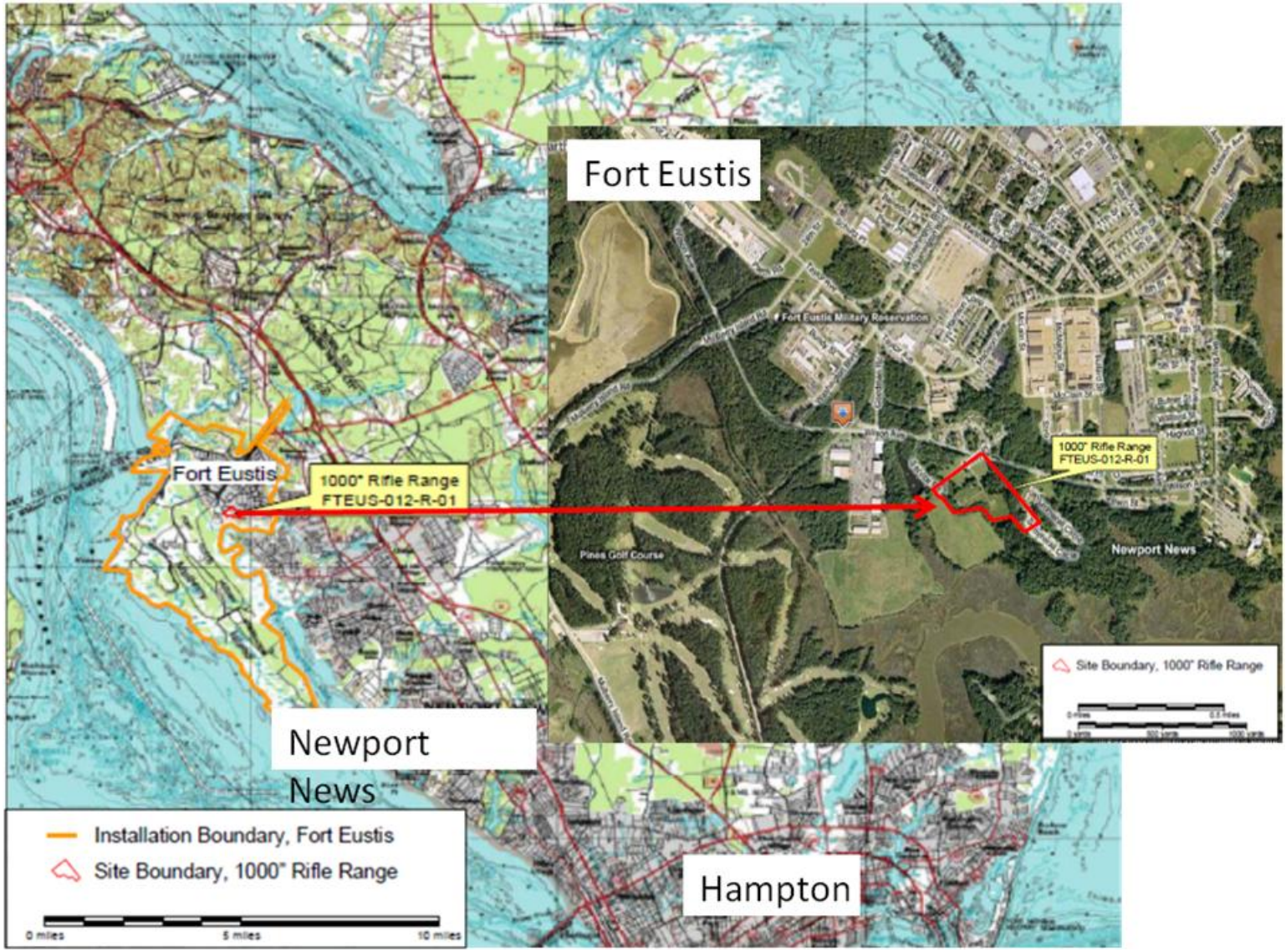

Figure 3. Map showing location of Fort Eustis, VA and 1000 inch rifle range.

4.1.3 Fort Wainwright

Fort Wainwright is located in central Alaska near Fairbanks and covers approximately 910,498 acres (Figure 4). The demonstration was conducted on the active Range 16 Records Range of the Fort Wainwright Small Arms Range Complex located off of (south) Richardson Highway. All manner of small arms ammunition is used on the Range 16 Record range.

Figure 4. Map of Fort Wainwright, Alaska and Range 16 Record Range.

4.2 SITE GEOLOGY/HYDROGEOLOGY

4.2.1 Kimama TS

The Kimama TS located in the Snake River Plain and the surface lithology consists largely of approximately 3 to 15 m thick sections of interbedded lacustrine and fluvial sediments of volcanic origin (Idaho Geological Survey, 2011). Soils are also volcanic in character and consist mainly of silt loam with some small areas of sandy loam. Analysis of two samples (KTS45 and KTS48) yielded a determination of poorly graded sand with silt (Clausen et al., 2013a). Some aeolian soil erosion has occurred in the vicinity of previous tank activity, particularly in the sandier soils (USACE, 1972).

The Kimama TS overlies the Snake River Aquifer, which occurs in basalt and sediments of the Snake River Group. The aquifer is located at an estimated depth of 100 – 150 m below ground surface. Groundwater flows most rapidly in the upper 60 m, which is the most productive portion of the aquifer and is associated with permeable zones consisting of the tops and bottoms of the basalt lava flows (USACE, 1972).

4.2.2 Fort Eustis

Fort Eustis lies within the Atlantic Coastal Plan and consists of unconsolidated and interbedded sands and clays with minor amounts of gravel and shell fragments. Locally, the site geology consists of impermeable clays, silts, and clayey sand with sand and silty sand lenses. Previous grain size analysis of soils from the 1000 inch Range were characterized as silty sand (URS, 2010), which is consistent with particle size sample (BCK1C) collected during this study (Clausen et al., 2013a). Groundwater is present at a depth of 4 to 6 m below ground surface with flow towards the Warwick River (URS, 2010). The 1000 inch Rifle Range drains through marshes into the Warwick River.

4.2.3 Fort Wainwright

The Fort Wainwright Small Arms Complex is located on surficial material consisting of well–stratified layers and lenses of unconsolidated sand and rounded river gravel overlain by as much as 5 m of silt. Gravel consists mostly of quartz and metamorphic rock with clasts ranging from 0.6 to 7 cm in diameter. The unit is 3 to more than 125 m thick. It is locally perennially frozen down to 90 m with low ice content. In addition, there are discontinuous swales and slough deposits consisting of poorly stratified lenses and layers of stream-laid silt and silty sand, which are well sorted and can contain up to 30% clay. These swale and slough deposits are locally perennially frozen with moderate to high ice content. Analysis of a surface soil from the study area (MI 15) yielded a particle distribution consistent with silty sand containing gravel (Clausen et al., 2013a).

4.3 CONTAMINANT DISTRIBUTION

4.3.1 Kimama TS

The munitions constituents (lead and antimony) were detected at levels during a SI warranting further investigation (FPM, 2009). Grab samples were collected in 2008. A subsequent RI/FS of the small arms range at Training Area 3 yielded no metal results exceeding USEPA screening criteria (FPM, 2010). However, only five composite samples were collected consisting of seven increments each from a radius of 0.3 meters (FPM, 2010). The composite sampling locations were selected at random; none of the samples were collected from the berm face, where the highest metal concentrations are expected. As discussed in Section 5.5.1, the ISM lead sample results collected from the berm face as part of our demonstration were slightly less than 300 mg/kg; the grab samples had a mean slightly less than 500 mg/kg.

4.3.2 Fort Eustis

The site is managed under the MMRP and had recently undergone a SI completed in 2007 (URS, 2007). The SI involved the collection of 24 shallow soil samples taken at depths of 0–12 in. in

the berms and firing lanes of the 1000 inch Rifle Range. All but four of these samples indicated lead concentrations were higher than the base-wide background level (23 mg/kg). Three of the soil samples had lead concentrations higher than the recommended soil screening level for residential use (400 mg/kg) - two in the Northern Berm and one in the Central Berm remnant.

4.3.3 Fort Wainwright

The small arms ranges at Fort Wainwright have not been previously sampled and analyzed for metals, principally because they are active ranges. Given the use of projectiles containing antimony, copper, lead, and zinc, the presence of these metals above background concentrations seemed likely.

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The experimental design for the demonstration was generally the same for all three sites and is described in Clausen et al. (2013a,b). The entire impact berm face for each site was considered the DU (Figure 5). Both the Kimama TS and Fort Eustis sites had a single intact berm (Figures 6 and 7). In contrast, the range at Fort Wainwright consisted of multiple (16) individual berms located at varying distances downrange from an individual firing point (Figure 8). At Fort Wainwright, samples were collected from all 16 berms at the 100 m downrange distance from the firing point to form the DU (Figure 9). In the case of Fort Wainwright, the firing point was also designated a DU and sampled using ISM to demonstrate that the methodology developed for metals was equally applicable to energetics, i.e., a single sample could be collected for both analyses. As the firing points at Kimama TS and Fort Eustis were no longer identifiable, samples were not collected from these areas during the demonstration (Clausen et al., 2013a).

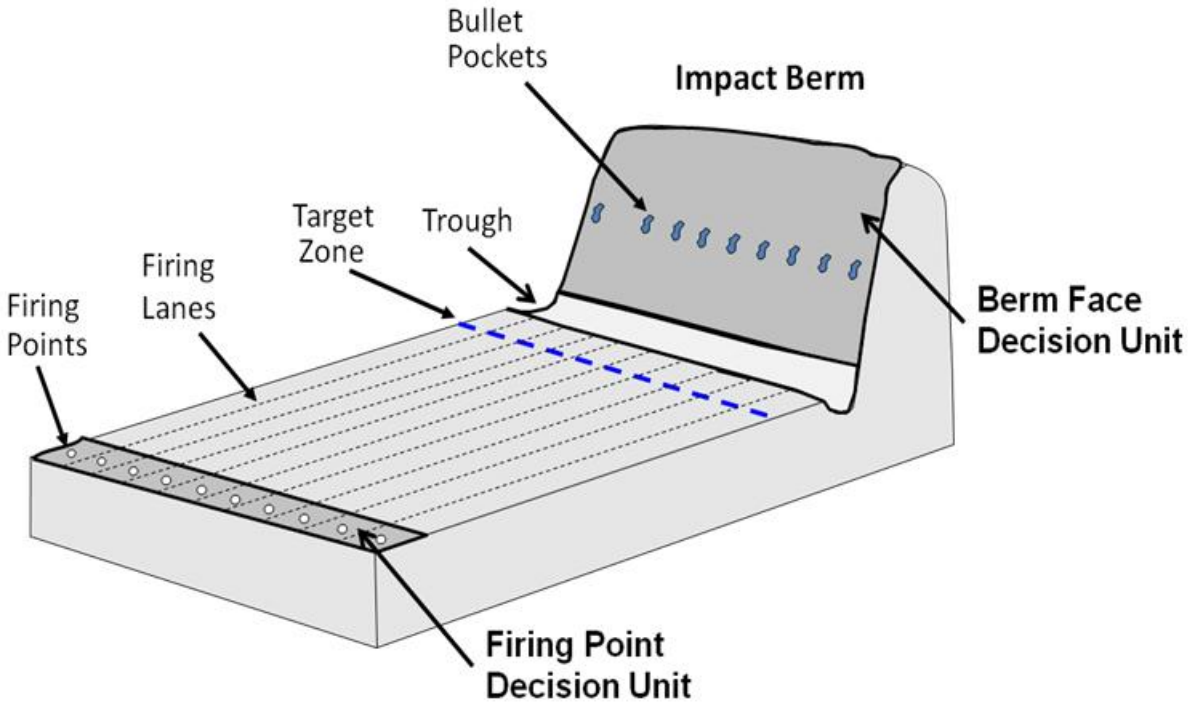

Figure 5. Generic example of a typical small arms firing range.

Figure 6. The northernmost small arms range berm face located in Training Area 3 of Kimama TS.

Figure 7. The 1000-inch small arms range berm face at Fort Eustis.

Figure 8. The small arms firing Range 16 Record berms at Fort Wainwright.

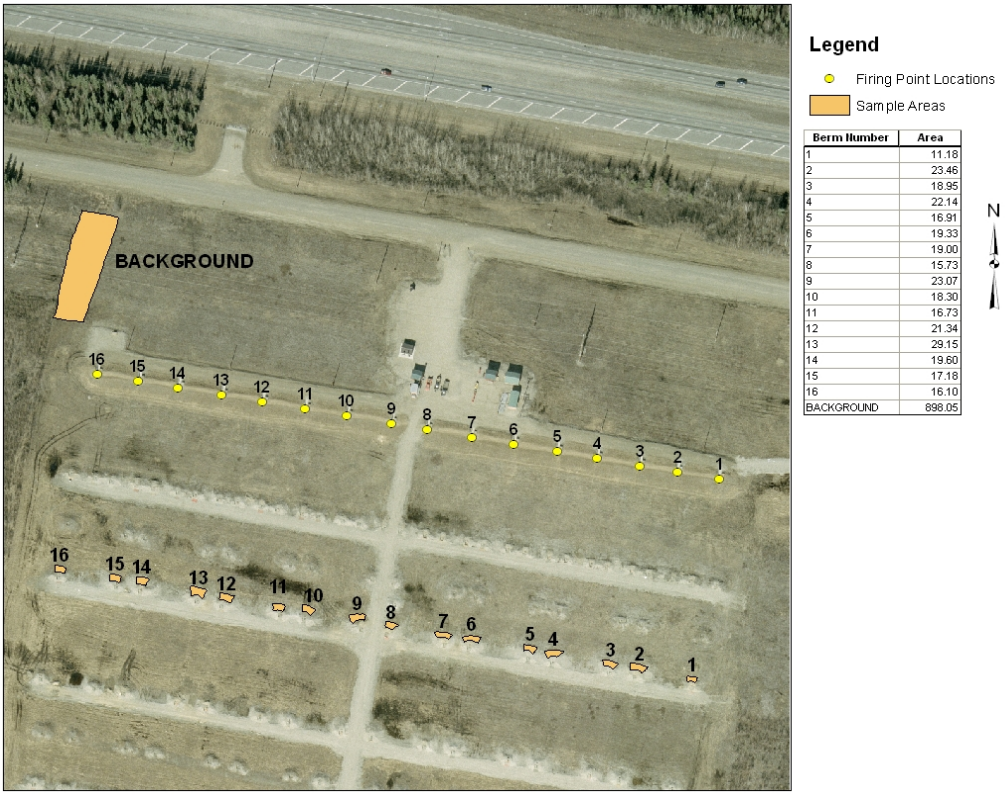

Figure 9. Location of berms sampled using ISM and grab techniques at the Range 16 Record Range at Fort Wainwright.

Using the random sampling approach, a total of 15 replicate ISM samples were collected from each berm face DU as well as the firing point DU at Fort Wainwright (Figure 1). Each replicate ISM sample consisted of approximately 100 increments. In the case of the berms at Fort Wainwright six increments were collected from each of the 16 berms (Figures 8 and 9). In addition, within each berm face DU, a grid was created and individual grab samples were collected. For each of the 16 individual berms three discrete samples were also collected using the pattern shown in Figure 10. In addition, the berms were subdivided into three SUs with samples pooled from the upper left, upper right, and lower bottom to look at the distribution of metal within the berm. Finally, Berm 11 was subdivided into two SUs (left and right) to determine whether the results for the right and left sides of the berm were similar.

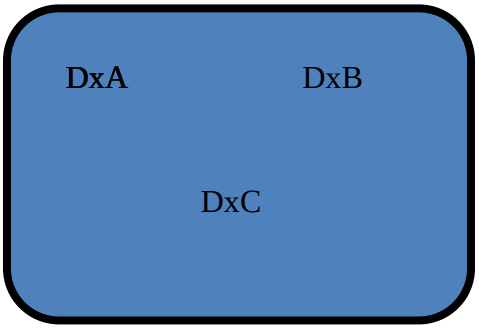

Figure 10. Grab sample grid layout for Fort Wainwright.

The grid sampling pattern used at the Fort Eustis and Kimama TS is shown in Figures 11 and 12, respectively. Two increments and two grab samples were collected per grid at Fort Eustis (Figure 13). The berm at Fort Eustis is a single DU that was divided into three SUs. Previous sampling (URS, 2007) indicated an area of elevated metal content on the northern end of the berm (Figure 13). Because the area was highly disturbed no background samples were collected at Fort Eustis. At the Kimama TS, a small arms range berm and background DU was established (Figure 14). Grab samples were also collected within the small arms range berm DU for comparison with the ISM samples.

1	2	3	4	5	6	7	8	9	10
11	12	13	14	15	16	17	18	19	20
21	22	23	24	25	26	27	28	29	30

Figure 11. Grab sample grid layout for Kimama TS berm face.

11	1	9	8	7	6	5	4	3	2	1
22	21	20	19	18	17	16	15	14	13	12
33	32	31	30	29	28	27	26	25	24	23

Figure 12. Grab sample grid layout for Fort Eustis berm face.

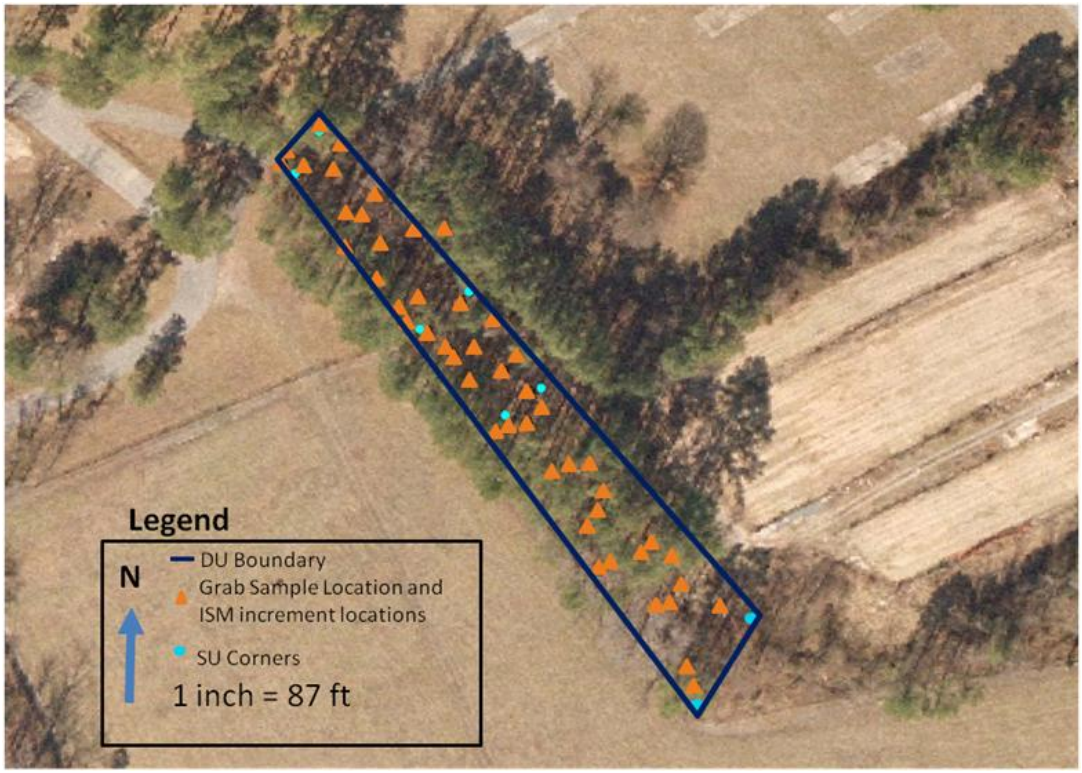

Figure 13. Aerial view of grab sample grid locations (orange triangles) and DU boundaries (blue circles) for the 1000 inch Rifle Range berm face at Fort Eustis.

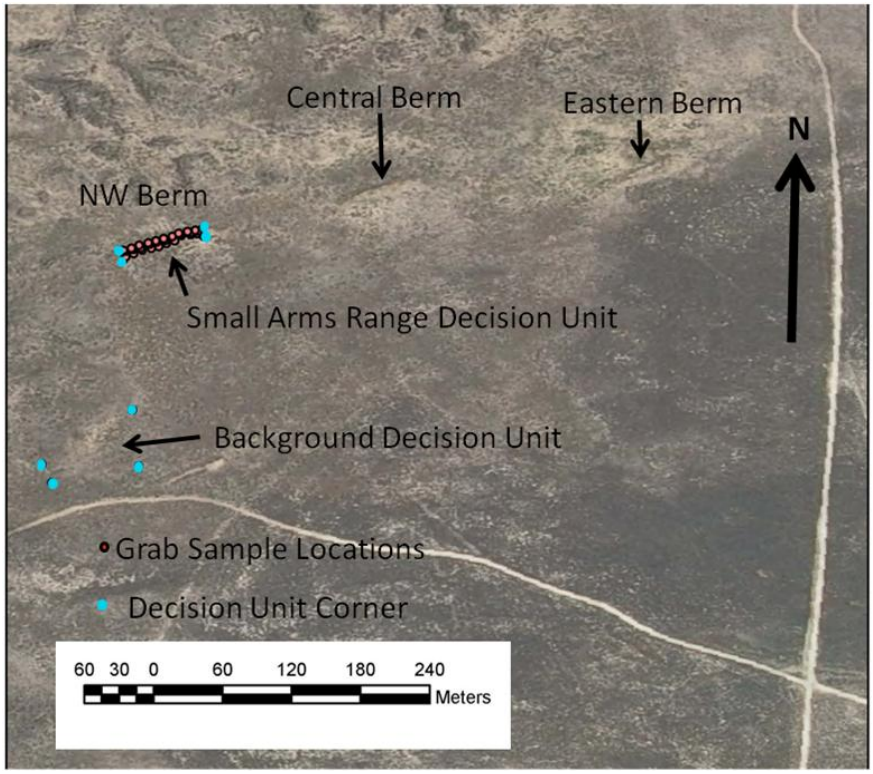

Figure 14. Aerial view of grab sample grid locations (orange circles) and DU boundaries (blue circles) for the NW berm face at Kimama TS.

5.2 BASELINE CHARACTERIZATION

Background surface soil samples were collected at Kimama TS and Fort Wainwright and analyzed for metals for comparison with samples obtained from the berm face and firing point DUs. A background sample was not collected from Fort Eustis because there did not appear to be any undisturbed soil locations in the vicinity of the range.

At the Kimama TS, the background samples did not have detectable concentrations of antimony (and thorium) (Clausen et al., 2013a). The concentration of copper ranged from 5.7 to 12.5 mg/kg with a mean of 8.0 mg/kg. Lead concentrations ranged from 5.2 to 1.2 mg/kg with a mean of 7.6 mg/kg.

At Fort Wainwright, the background samples did not have detectable concentrations of antimony (as well as silver, beryllium, cadmium, and thorium) (Clausen et al., 2013a). The concentration of copper ranged from 16.7 to 28.8 mg/kg with a mean of 26.8 mg/kg. Lead concentrations ranged from 8.1 to 136 mg/kg with a mean of 63.7 mg/kg.

In addition to the metal content of the background samples, several additional physical and chemical characteristics for the native soils were determined including grain size, total organic carbon (TOC), cation exchange capacity (CEC), and soil pH (Clausen et al., 2013a).

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

The results from earlier laboratory studies under Task 1 of this project (Clausen et al., 2012b) were presented in the final report. No new treatability or laboratory studies were conducted for this demonstration.

5.4 FIELD TESTING

There are four basic field phases to ISM: 1) project planning, 2) mobilization, 3) surveying/sampling, and 4) demobilization (Table 6). A draft demonstration report was submitted to ESTCP in June 2013 (Clausen et al., 2013a) followed by a protocol for ISM implementation at small arms ranges (Clausen et al., 2013b). The project planning phase involves developing the conceptual site model, determining the study objectives, identifying the data needs, establishing the DU, and defining the depth and number of increments per ISM sample. Mobilization involves gathering the field equipment together and traveling to the site. The surveying/sampling phase involves demarcating the DU in the field, surveying the DU boundary or a corner of the DU, and sampling. The first three phases are identical to current conventional sampling methods. Sampling involves collection of conventional grab samples from within the DU as well as collection of ISM samples. Demobilization involves packing up the sampling equipment, shipping samples back to the laboratory, and travel. Again, this is no different than the current conventional method. No investigative derived waste is created nor is equipment left at the sites.

Table 6. Gantt chart for field demonstration activities.

Activity	September 2011			October 2011				November 2011				December 2011				
	12-16	19-22	26-30	3-7	11-14	17-21	24-28	31-4	6-10	14-18	21-23	28-2	5-9	12-16	19-23	27-30
Fort Wainwright																
Project Planning																
Mobilization																
Surveying/Sampling																
Demobilization																
Kimama TS																
Project Planning																
Mobilization																
Surveying/Sampling																
Demobilization																
Fort Eustis																
Project Planning																
Mobilization																
Surveying/Sampling																
Demobilization																

Each ISM sample consisted of collecting approximately 100 increments within a DU using systematic random sampling (Figure 1). A DU was established at the firing point (Fort Wainwright) and berm face of each small arms range. Firing points could not be established for the Fort Eustis or Kimama TS (Clausen et al., 2013a). The firing point DU at Fort Wainwright extended 5 m behind and 5 min front of the firing point and encompass all firing lanes at the small arms range. The berm face DUs encompassed an area including all firing lanes as well as from the base of the berm face to the top. In addition, at Fort Eustis, three SUs within the DU were established for comparison with previous contractor conducted SI studies. At Fort Wainwright, a continuous berm is not present so the 16 individual berms located at 100 m down range from the firing point were considered a contiguous berm. The area sampled represented approximately 0.5 acres. Within each DU, approximately 100 evenly spaced increments were collected to form an individual ISM surface soil sample. The CMIST (Walsh M.R., 2009) was used to extract cylindrical soil cores referred to as "increments." The coring bit used had a diameter of 2 cm. The sampling depth used at all three sites was 5 cm, which yielded an ISM sample of approximately 1-2 kg. The required mass is a function of the soil volume of each core (the sampling depth and core diameter), the number of cores/increments collected, and the mean soil density. While the typical approach is to collect three replicate ISM samples for each DU to assess uncertainty, this demonstration collected 15 replicate samples to facilitate statistical comparisons between the ISM and grab sample results.

Using a grid-node approach, 48 grab samples were collected from Fort Wainwright, 33 were collected from Fort Eustis, and 30 grab samples were from Kimama TS (Clausen et al., 2013a). From within each node, a single increment was collected using the CMIST sampler and placed in individual amber 4 oz containers yielding a sample mass of approximately 0.2 kg. Typically, grab samples would be collected with a metal scoop. However, for direct comparison between the ISM and grab samples the same sample device, CMIST, was desired. For a typical small arms range a half-dozen to dozen grab samples would typically be obtained. However, to facilitate statistical analysis of the data and comparisons with the ISM data more samples were collected than is typical (> 30). The grid-node layout encompassed the same area as the DUs where the ISM samples were collected.

5.5 SAMPLING METHODS

The demonstration included collection of 63 ISM surface soil samples and 50 conventional grab samples at Fort Wainwright; 18 ISM and 30 grab samples from Kimama TS; and 27 ISM and 33 grab samples at Fort Eustis (Clausen et al., 2013a). Conventional grab and ISM samples were collected from three small arms range berm DUs at each of the military installations. One firing point DU sample was collected at Fort Wainwright to assess the suitability of collecting and processing a single sample for both metal and energetic analysis. A boundary for each DU was determined in the field largely based on the observable extent of the impact berm or firing point.

5.5.1 Grab Samples

Grab surface soil samples were collected following the conventional grid node approach from within each DU. All grab sample locations were individually surveyed. Instead of using a metal scoop, the CMIST was used to collect the grab sample from the center of the grid. The 2 cm diameter corer was used with a 5 cm deep sample collected. The grab samples were processed following the USEPA Method 5030B, which basically involved scooping a 1 g sample out from

the top of the sample jar and then performing the standard digestion. Metals analysis followed USEPA Method 6010.

5.5.2 Incremental Sampling Methodology Samples

Collection of ISM surface soil samples followed the methodology outlined in Section 2.1 Technology Descriptions (Clausen et al., 2013a) and the steps including sample preparation are summarized in Table 1 with the differences between ISM and conventional grab approaches shown in Table 7. The ISM samples were collected in plastic bags by combining 100 increments with a total mass of 1- 2 kg. All samples for this demonstration were processed and extracted/digested at CRREL. Samples were analyzed following USEPA Method 8330B for Nitroglycerine (NG), 2, 4-dinitrotoluene, and 2, 6-dinitrotoluene, or a modified Method 3050B/6010B for metals. Energetic analysis was performed at CRREL and all metals analysis and additional analytes were analyzed at the Environmental Laboratory (EL).

A background location close to the small arms ranges at each installation but upwind of the prevailing wind direction was located, except for Fort Eustis. Triplicate (n = 3) 100 increment samples were collected from these background DUs, which covered an area of 0.5 acre at each site.

At Fort Wainwright, 15 replicate ISM samples were collected from the firing point and analyzed for energetics and metals. The intent was to demonstrate the metals ISM process will work with soils containing energetics. For each berm DU, n = 15 ISM field replicates were collected to evaluate total precision.

Table 7. Comparison of Grab versus ISM for this demonstration.

Activity	Conventional Grab Sampling	Incremental Sampling Method
Surveying	Each individual sample location was flagged and surveyed.	The DU corners were determined and demarcated with flagging as were lane boundaries for sample collection. The four corners of the DU were surveyed.
Soil sampling	• Not explicitly addressed in Method 3050B. • Grab samples collected with CMIST from biased locations . • Typically, about 200 g soil was collected in 4 oz. wide mouth amber screw top jars.	A 100 increment sample was collected randomly over the entire DU (e.g., using a systematic sampling) using CMIST. Typically, 1-2 kg of soil in clean large (e.g., 15 ×15 inches, 6 mm thick) polyethylene plastic bags sealed with Ty-wraps.
Sample Drying	Not performed	Samples were air-dried at room temperature by spreading it onto tray to form a relative thin uniform slab.
Sieving	Not performed	Samples were passed through a #10 (2 mm) sieve. Both size fractions were weighed and < 2 mm fraction is additionally processed.
Milling	Not performed, although disaggregation with a mortar and pestle is sometimes performed	Samples were milled using a Puck Mill for 5 x 60 seconds.
Laboratory sub-sampling	A single aliquot was scooped from the top of the container for digestion and analyses.	After milling the soil was spread onto a large tray to form a thin slab of material of uniform thickness, at least 20 small aliquots “increments” were randomly collected over the entire slab with a flat spatula to prepare a sub-sample for digestion and analysis.
Sub-sample mass	1g wet weight	2 g dry weight
Analysis	EPA Method 6010	EPA Method 6010 (USEPA Method 8330B for Firing Point sample from Fort Wainwright).

5.6 SAMPLING RESULTS

5.6.1 Kimama Training Site

At the Kimama TS copper and lead were detected in ISM surface soil samples from the small arms Northern Berm in Training Area 3 at levels higher than the background sample. The mean copper and lead levels in the background ISM sample were 7.96 and 7.61 mg/kg, and 35.3 and 292 mg/kg in the berm sample, respectively (Clausen et al., 2013a). In contrast, the mean copper and lead results for the grab samples were 23.0 and 493 mg/kg, respectively (Figure 15) indicating the grab sample mean for lead (493 mg/kg) was nearly double that of the ISM mean (292 mg/kg). Note, the ISM mean and median for lead are nearly the same (292 versus 287 mg/kg), whereas the mean and median lead grab sample values (493 versus 73.5 mg/kg) differ by nearly a factor of seven. A total of 15 replicate ISM and 30 grab samples were collected and the calculated RSD for lead was significantly higher for the grab samples (334%) as compared to the ISM samples (18%). The individual grab results for the berm face are depicted in Figure 15. The western side of the Northern Berm had higher Cu, Pb, and Zn concentrations than the eastern side of the berm. Individual sample results for all ISM and grab samples including all metal analytes are provided in Clausen et al. (2013a).

Lead Results for Discrete Samples (mg/kg)											**Legend**
	75	1240	9060	1050	523	278	103	60	85	45	<50
	39	287	97	325	556	278	72	31	24	14	51-299
	11	19	30	40	142	198	28	49	25	13	>300
	ISM Mean = 292, ISM Median = 287, Discrete Mean = 493, Discrete Median = 73.5										
Copper Results for Discrete Samples (mg/kg)											
	20	57	74	32	41	42	26	15	18	18	<20
	14	24	21	19	39	42	14	16	13	13	21-39
	10	10	12	14	14	22	13	18	11	12	<40
	ISM Mean = 35., ISM Median = 29.2, Discrete Mean = 23.0, Discrete Median = 18.1										
Antimony Results for Discrete Samples (mg/kg)											
	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	2.2	<2.00	<0.02
	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	>0.021
	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	
	ISM Mean = <2.00, ISM Median = < 2.00, Discrete Mean = 19.5, Discrete Median = 3.01										
Zinc Results for Discrete Samples (mg/kg)											
	53	53	56	46	55	51	48	41	47	41	<25
	54	52	45	50	42	51	22	43	40	39	26-49
	45	44	42	46	44	51	44	42	37	40	>50
	ISM Mean = 30.0, ISM Median = 28.9, Discrete Mean = 45.4, Discrete Median = 44.9										

Figure 15. Grab surface soil results for lead, copper, antimony, and zinc (mg/kg) from the Kimama TS small arms range berm face with ISM comparisons.

5.6.2 Fort Eustis

At the 1000 inch Firing Range on Fort Eustis, copper and lead levels were elevated in grab and ISM surface soil samples for the entire berm face (Clausen et al., 2013a). The mean copper and lead grab sample results were 43.3 and 434 mg/kg, respectively, whereas, the mean ISM results were 51.2 and 496 mg/kg, respectively. Unlike the Kimama TS results, the mean values for the grab and ISM samples are similar for both copper and lead. Although the ISM mean and median for lead values are nearly the same (496 versus 509 mg/kg), the mean and median lead grab

sample values (434 versus 94.3 mg/kg) differ by nearly a factor of five, indicating the grab sample results are highly skewed. A total of three replicate ISM and 33 grab samples were collected and the calculated RSD for copper and lead was significantly higher for the grab samples (298 and 350%, respectively) as compared to the ISM samples (104 and 72%) indicating greater precision with the ISM versus grab samples. The performance criteria of <30% RSD was not met with the ISM samples suggesting an insufficient sample mass resulting from an insufficient number increments per sample, insufficient mass per increment collected, or an insufficient mass of for the digestion aliquot.

Because previous SI data indicated most of the copper and lead was concentrated on the right side (Hotspot 1) of the berm (URS, 2007) a focused sampling effort was conducted in this area as well. A total of 12 grab and 15 ISM samples were collected from the first four grids (northern side of Figure 13). The mean grab sample copper and lead results were 93.5 and 1,002 mg/kg, respectively (Clausen et al., 2013a). The mean ISM copper and lead results were 114 and 932 mg/kg, respectively. Similar to the observation for the full berm, the ISM mean and median lead values were nearly the same 932 and 934 mg/kg, respectively. In contrast, the mean and median lead values for the grab samples were significantly different, 1,002 and 212 mg/kg respectively, indicating a highly skewed dataset. An assessment of the precision of results indicated that the grab samples (n=12) had RSDs of 224%, 241%, and 166% for copper, lead, and zinc, respectively. In contrast, the RSD for the ISM data (n=14) yielded values of 44%, 30%, and 4% for copper, lead, and zinc, respectively. Individual sample results for all ISM and grab samples including all metal analytes are provided in Clausen et al. (2013a). Copper did not meet the performance objective of < 30% RSD suggesting a longer milling interval or larger digestion aliquot mass may be necessary for improved sample precision.

These results indicate there is a large, long-range spatial heterogeneity of metallic residues. The results from the three SUs indicate most of the metal contamination is present in the northern end of the berm, an observation that would likely not have been apparent (e.g., without historical knowledge) if a small number of grab samples (e.g., n = 10) were collected in a judgmental manner to characterize the berm. The long-range spatial heterogeneity and the large variability (e.g., RSDs) of grab sample results suggest the mean concentration of the entire berm will likely not be accurately estimated without collecting a large number of grab samples over the entire berm (e.g., using systematic random sampling).

5.6.3 Fort Wainwright

At the Range 16 Record Range at Fort Wainwright, copper and lead levels in the background surface soil samples appear to be at similar levels as the ISM entire berm sample suggesting the background location selected behind the firing point has been anthropogenically impacted. The mean copper and lead levels in the background ISM sample were 38.2 and 416 mg/kg, respectively (Clausen et al., 2013a). In contrast, the mean copper and lead levels in the ISM firing point sample were 135 and 50.5 mg/kg, respectively, and at the berm 92 and 453 mg/kg, respectively. In addition to the metals, NG was detected at the firing points with a mean concentration of 335 mg/kg. The RSDs for metals and NG for replicate firing point incremental samples met the target value of 30% for total precision. The measurement performance objective of the incremental samples that were collected from the berm was also met for lead and zinc. However, the RSD for copper was 64%. It has been our observation that copper has a tendency

to plate out in the Puck Mill. It is possible that a longer milling interval, greater than 300 seconds, would result in better precision.

The mean copper, lead, and antimony grab sample results for the entire berm were 81.0, 432, and 14.0 mg/kg, respectively (Clausen et al., 2013a). The lead grab samples mean (432 mg/kg) for the entire berm was similar to the ISM mean (453 mg/kg). The entire berm ISM mean and median for lead are nearly the same (453 versus 468 mg/kg). The mean and median lead grab sample values (432 versus 85.7 mg/kg) differ by nearly a factor of five, indicating the grab sample results are highly skewed.

A total of 15 replicate ISM and 48 grab samples were collected. The calculated grab sample RSDs for copper lead, and zinc were 218%, 228%, and 42%, respectively (Clausen et al., 2013a). In contrast, the calculated copper lead, and zinc RSDs for the ISM samples were 64%, 24%, and 12%, respectively. Individual sample results for all ISM and grab samples including all metal analytes are provided in Clausen et al. (2013a).

6.0 PERFORMANCE ASSESSMENT

6.1 SAMPLE REPRODUCIBILITY WITH INCREMENTAL SAMPLE METHODOLOGY

A quantitative performance objective for ISM was to obtain reproducible sample results through collection and analysis of replicate field samples. Two different statistical success criteria were developed for this evaluation. The first approach involves collecting replicate incremental samples and grab samples in the same DU and subsequently using statistical hypothesis tests to determine whether the ISM approach results in significantly smaller variances. The smaller ISM variances were compared with the grab variances to determine whether they are significantly different with at least 95% confidence. The evaluation indicated the ISM approach generally resulted in better measurement precision for all three of the demonstration sites; the ISM approach generally resulted in smaller variances, though the target level of confidence (95%) was not met for all of the metals and DUs. The largest differences in the variance were observed for lead, which is usually the primary contaminant of concern for small arms ranges. The large reductions for the lead variances is illustrated in the plots below for the natural-logarithm-transformed ISM (n = 15) replicates and the (n = 48) grab replicates from the Fort Wainwright DU. The Levene's test indicates the variance of the set of incremental samples (denoted as "ISM") is significantly smaller than variance of the set of grab samples (denoted by "Discrete") with well over 95% confidence (as the "P-value" is much smaller than 0.05).

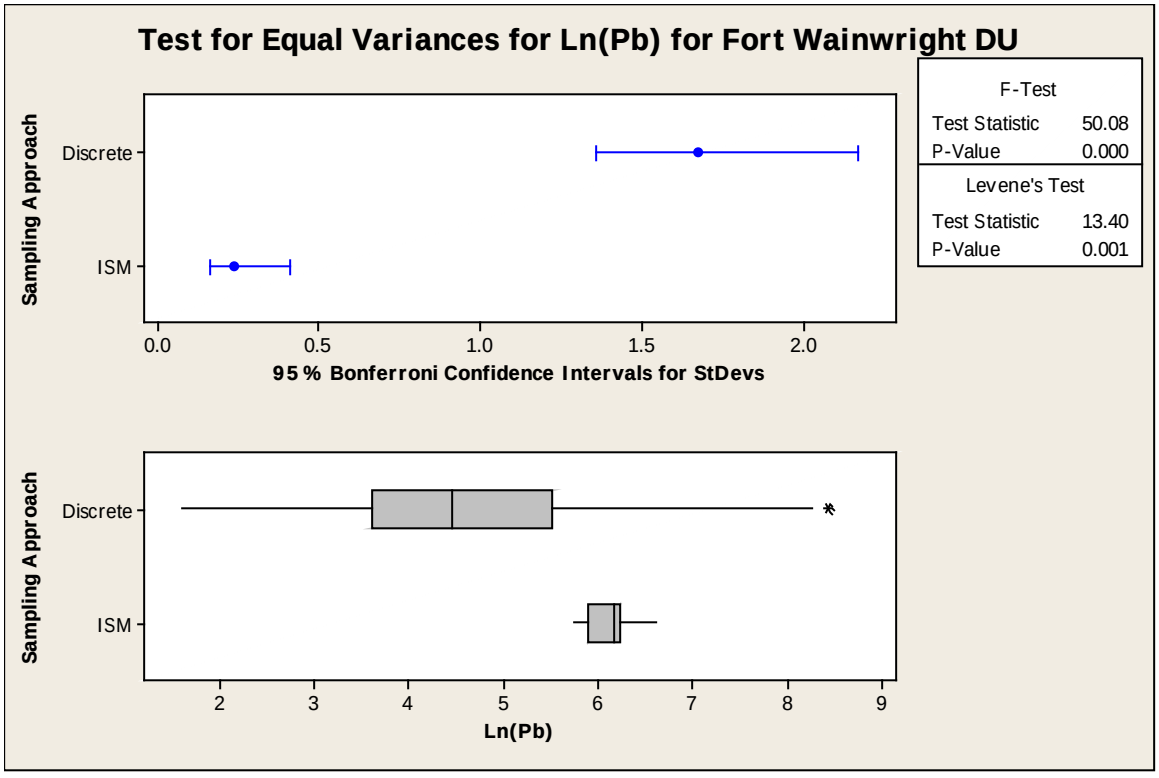

Figure 16.

The Levene's test was not able to detect significant differences between the grab and ISM variances for copper and zinc with at least 95% confidence, but the square ranks test for the variances detected significant differences with at least 95% confidence for lead and copper (the level of confidence was > 99% for lead, 99% for copper but only 85% for zinc). Although the hypothesis tests did not detect significant differences between the variances at the target level of confidence, the ISM approach seems to result in better precision than conventional grab sampling. The standard deviation for the set of grabs (22 mg/kg) is over three times larger than the ISM standard deviation (7 mg/kg). As shown in the zinc box plots below, the grab replicates also exhibit greater skewness than ISM replicates. Values that exceeded the upper or lower quartiles by 1.5 x interquartile Range (IQR) or more were identified as "outliers," consistent with conventional terminology and plotting procedures for box plots.

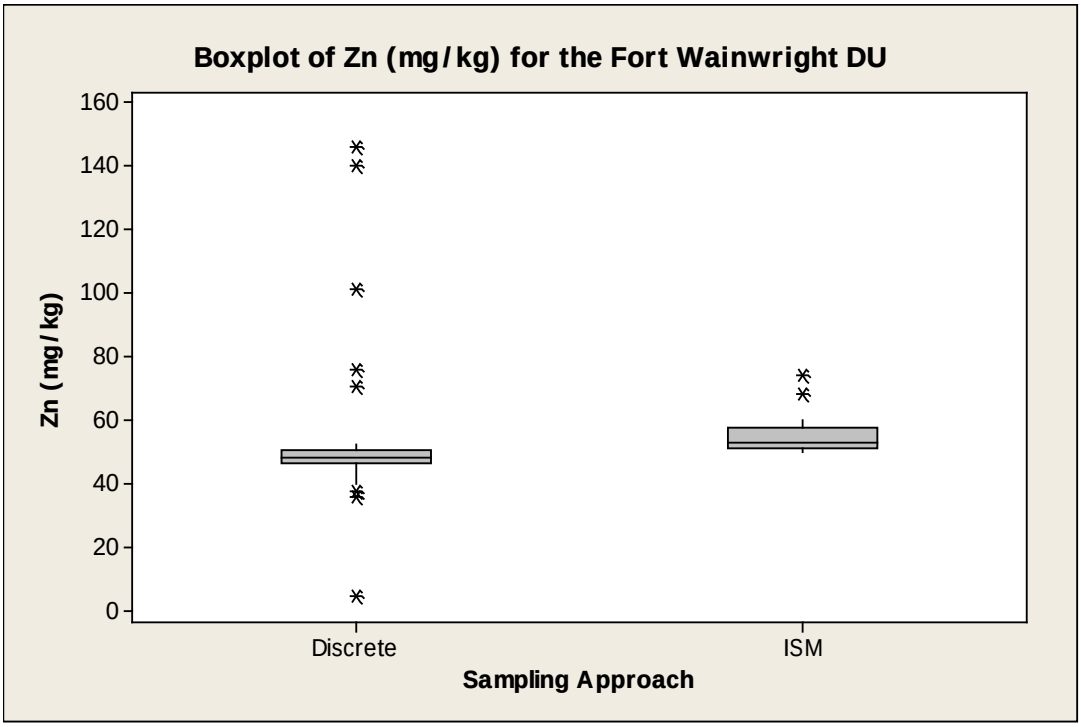

Figure 17.

A second qualitative evaluation involved calculating the RSD for each population (Table 8). Again, for all three sites the RSDs for the ISM samples were significantly lower than the conventional grab samples with a few situations where the measurement performance objective of < 30% RSD was not met for some metals with ISM. As shown at Fort Eustis and Fort Wainwright, an ISM sample with a larger number of increments and greater mass yielded lower RSDs (Table 8). It is believed in those situations where the performance metric of RSD <30% was not met that the target would have been achievable with the following: by re-sampling and collecting an ISM sample with a greater number of increments, by using a larger sampling tool to increase the recovered mass, by increasing the digestion mass, or by increasing the number of sub sampling increments to build the digestion aliquot. This leads to the observation that when the degree of expected analyte heterogeneity is unknown the sampler should err on the conservative side by collecting a sample from a DU with a larger number of increments or

greater mass. The other approach is to select a DU with a smaller area that will thus increase the increments/DU area or mass of sample/DU area. Overall, sample reproducibility precision was improved with the collection of ISM samples compared with conventional grab samples. Laboratory sub-sampling precision was previously demonstrated during the technology development of this project (Clausen et al., 2012b, 2013a).

Table 8. Comparison of relative standard deviations for the analytes of interest (copper, lead, antimony, zinc) for ISM and conventional grab samples at three demonstration sites.

	Kimama TS	Fort Eustis[1]	Fort Wainwright[2]
Incremental Sampling Methodology			
Mean mass (g)	881	1112/1485	2403/1208/1237
Number of Samples	15	15/15	15/15/15
Copper RSD (%)	53	104/44	64/52/125
Lead RSD (%)	18	72/30	24/56/58
Antimony RSD (%)	ND	500/60	ND/ND/ND
Zinc RSD (%)	23	5/4	8/17/20
Conventional Grab Samples			
Mean mass (g)	100	78.8/69.6	159
Number of Samples	30	33/12	48
Copper RSD (%)	66	298/224	218
Lead RSD (%)	334	350/247	226
Antimony RSD (%)	172	219/295	97
Zinc RSD (%)	15	23/27	69

Green = <30% RSD, Yellow = ~ 30% RSD, Red = > 30% RSD
RSD – relative standard deviation, ND – not detected
[1] entire berm/right side of berm,
[2] entire berm/ left side Berm 11/right side Berm 11

6.2 BIAS EVALUATION

Clausen et al. (2013a) evaluated the method blanks and LCS for bias with none indicated. Glass blank samples analyzed as a control indicate some increase in aluminum, chromium, iron and manganese as a result of milling with the Puck Mill, although none of the analytes of interest (copper, lead, antimony, or zinc) increased significantly (Clausen et al., 2012b, 2013a), which is consistent with the findings of Felt et al. (2008) for reference soils studied. Therefore, there is no significant cross-contamination from the Puck Mill into the samples for the metals of interest (copper, lead, antimony, or zinc).

6.3 PERFORMANCE COMPARISON

As demonstrated in Clausen et al. (2012b), measurement of the improved accuracy as compared to the "true" mean is difficult to quantify, because the true mean is typically unknown. Either knowing the total amount of metal introduced into the DU or digestion of all the soil in the DU are the only means to know the true metal concentration. Neither of these are practical approaches because the number of projectiles fired into a berm DU is typically unknown and it is not practical to digest several hundred/thousand kilograms of soil. The approach taken in Clausen et al. (2012b, 2013a) was to pool all of the ISM samples from a DU to calculate the overall mean. The assumption is that the pooled mean is more representative of the true site condition. This assumption is not entirely unreasonable as the DUs studied typically had several

dozen ISM samples collected with each ISM sample containing 50 to 100 increments. Thus, the total number of increments collected from a given DU was several hundred up to 1500 in one instance. Comparing the pooled ISM mean to the grab sample results indicated accuracy errors approaching 100% for individual grab samples. The only means to reduce the accuracy error with grab samples was to increase the number of grab samples collected.

As shown in this demonstration (Table 8), total sample error or precision as measured qualitatively using the RSD is often several hundred percent for conventional grab samples whereas RSDs for ISM samples are typically <30% for soils containing metallic residues (Clausen et al. 2013a,b).

Improved accuracy or precision may not been necessary when the soil metal concentration is well above or below a regulatory action level or some other criteria for comparison. However, when the measured soil concentration is close to an actual level the precision and accuracy of the measurements becomes increasingly important. As observed from this demonstration, in the case of lead, different decisions are likely to be made whether conventional grab or ISM samples are collected. Clausen et al. (2013a) provides an example for lead at the Fort Wainwright Record Range berm where different decisions could be made when relying on the grab sample data alone. Whereas a consistent decision would be made each time if the ISM data is used. Assuming a regulatory action level of 400 mg/kg for lead 13% of the time the grab sample value would be < 400 mg/kg and 87% of the time would be > 400 mg/kg. However, the ISM data clearly indicates the mean lead level for the DU is above 400 mg/kg. Consequently, reliance on grab samples would result in a relatively high false negative rate (i.e., erroneously concluding contamination is less than the 400 mg decision limit for remedial action).

In terms of assessing performance by cost, each stage of the sampling activity and laboratory processing step was evaluated for the time to perform the task for both the ISM and conventional grab samples at each of the three sites. For the field sampling activities, seven variables were considered for surface soil samples: 1) mobilization preparation time, 2) shipping of field equipment to the site, 3) surveying/flagging in the field, 4) sampling, 5) labeling of samples, 6) demobilization, and 7) shipping of samples to the laboratory and equipment. Mobilization, shipping equipment to the field, and demobilization costs are essentially the same. The remaining field activities take twice as long with ISM versus conventional grab sampling on a per sample basis. Laboratory preparation procedures assessed for the soil samples were: 1) air drying, 2) sieving, 3) milling, and 4) sub-sampling to prepare the digestion aliquot. With the conventional grab sampling approach the collection of a 0.5 to 2 g aliquot from the top of the jar takes minimal time, thus there are no sample preparation costs. Based on experience at CRREL the laboratory, preparation time per sample is roughly 30 minutes of labor. There is essentially no difference between analyses for a conventional grab sample versus ISM. The breakdown of costs, based on a field technician and laboratory technician at a rate of $50/hr by field, sample preparation, and analysis activity is shown in Table 9. On a per sample basis, the cost of ISM is approximately 55 to 65% higher than conventional grab sampling. However, a cost savings is apparent when one considers the number of samples. The more grab samples needed to characterize the DU (7 versus 15 grab samples), the more favorable the cost comparison with ISM (Table 9). For a typical small arms range DU, three replicate ISM samples would be commonly collected versus 7 to 15 conventional grab samples for the same DU. Thus, the total

project cost is 1 to 3 times (5 to 65% higher) with the conventional grab sampling method versus ISM. Therefore, ISM met our performance criteria of at least a 20% reduction in sample cost even when the quality of the grabs results (e.g., the poorer measurement precision) relative to set of incremental samples is not taken into account.

Table 9. Comparison of costs between ISM and conventional grab sampling on a per sample and total cost basis based on demonstrations at Kimama TS, Fort Eustis, and Fort Wainwright.

Activity	Per Sample Costs ($)		Total Project Costs ($)		Total Project Costs ($)	
	ISM	Grab	ISM[1]	Grab[2]	ISM[1]	Grab[3]
Field	35 - 50	10 - 15	105 - 150	70 - 105	105 - 150	150 - 225
Laboratory Preparation	40 - 60	0 - 10	120 - 180	0 - 70	120 - 180	0 - 150
Analysis	225 - 275	125 - 135	675 - 825	875 - 945	675 - 825	1875 - 2025
Total	**300 - 385**	**135 - 160**	**900 - 1155**	**945 - 1120**	**900 - 1155**	**2025 - 2400**

[1] Based on collection of 3 replicates
[2] Based on the collection of 7 grab samples
[3] Based on the collection of 15 grab samples

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7.0 COST ASSESSMENT

The costs associated with field-sampling activities include travel, related lodging and meals, labor, and the shipment of samples off site. Unique to the costs associated with sampling activities on military training ranges is the need to acquire the services of explosive ordnance disposal (EOD) personnel or UXO technicians. However, the expenses associated with gaining site assess, engaging EOD support, travel, and labor are anticipated to be equivalent for grab and ISM. Additionally, in the case of small arms ranges, an EOD escort is not needed because UXO presence is unlikely. The major cost differences between ISM and conventional grab sampling thus arise predominately from the ISM requirement of handling and processing of larger environmental samples. However, this cost increase is greatly offset by the need for fewer ISM samples than grab samples to adequately characterize a DU. The cost differential between conventional grab samples and ISM is quantifiable. However, the cost of making an incorrect decision is not easily quantifiable. The potential cost of implementing a remedial remedy when it is not necessary could be quite large, ranging from tens of thousands to tens of millions of dollars. The potential remedial action of a false positive finding is not likely to be known, unless both conventional grab and ISM samples are collected. However, implementation of ISM will result in lower false positive rate, which is associated with fewer unnecessary remedial actions. Conversely, the ISM also has a more reliable detection rate, thus avoiding false negatives.

7.1 COST MODEL

To aid our cost analysis, the labor hours in all phases or actual costs of the field demonstration (site preparation, locating the sample with Global Positioning System (GPS), sample labeling, sample collection, shipment of samples, etc.) were collected and tracked in an Excel spreadsheet (Clausen et al., 2013a; Table 10). In addition, the cost or labor hours to process the samples and analyze them in the laboratory were tracked. Labor categories and labor rates were ascertained so that labor hours can be converted to actual costs. Because the actual number of samples collected for this demonstration is greater than a typical project, the following approach was taken. Three ISM replicate samples from a single DU were compared against a typical number of conventional grab samples for the same DU. Because the number of grab samples collected varies by objective, analyte of concern, desires of the interested stakeholders, etc., two scenarios were considered: 7 and 15 grab samples. This range was based on discussions with individuals involved with sampling MMRP sites using conventional grab sampling techniques.

We also calculated the costs based on our labor at CRREL/EL for sample preparation and analysis and obtained actual costs from several commercial environmental laboratories (Table 11). A labor rate of $50/hr was used for converting labor into dollars. A typical soil digestion and target analyte list (TAL) analysis of 13-18 metals by a commercial environmental laboratory costs $100/sample. If ISM sample preparation (air drying, sieving, sub-sampling) including milling is required this adds approximately $125/sample, based on discussions with several commercial environmental laboratories. Use of ISM sample preparation without milling adds approximately $75/sample.

Table 10. Comparison of labor hours[1] or costs by cost element between ISM and conventional grab sampling on a per sample and total cost basis based on demonstrations at Kimama TS, Fort Eustis, and Fort Wainwright.

		Fort Wainwright				Fort Eustis				Kimama TS			
		ISM	Grab	ISM	Grab	ISM	Grab	ISM	Grab	ISM	Grab	ISM	Grab
Stage	Activity	Per Sample		Total Project		Per Sample		Total Project		Per Sample		Total Project	
Mobilization	Preparation	=	=	=	=	=	=	=	=	=	=	=	=
	Expendables	$8.62	$1.29	$129.35	$61.92	$8.62	$0.89	$129.35	$42.57	$8.62	$1.29	$129.35	$38.70
	Shipping Field Equipment	=	=	=	=	=	=	=	=	=	=	=	=
Field	Surveying/Flagging	1	1	16	53	2	1	30	45	1	2	8	54
	Sampling	12	2	90	37	20	4	150	60	20	3	150	45
	Decontamination	0	2	0	96	0	5	0	165	0	5	0	150
	Labeling	2	2	35	113	1	1	15	33	1	1	18	36
	Demobilization	=	=	=	=	=	=	=	=	=	=	=	=
	Shipping Samples	$25.27	$2.46	$379.00	$118.00	$7.54	$2.59	$113.14	$85.47	$22.27	$3.67	$334.00	$110.00
	Shipping Field Equipment	=	=	=	=	=	=	=	=	=	=	=	=
Laboratory	Air Drying Prep	2	0	30	0	2	0	30	0	2	0	30	0
	Sieving	2	0	30	0	2	0	30	0	2	0	30	0
	Milling	5	0	75	0	5	0	75	0	5	0	75	0
	Cleaning Milling Equipment	10	0	150	0	10	0	150	0	10	0	150	0
	Sub-Sampling	10	0	150	0	10	0	150	0	10	0	150	0
	QA/QC	$26.67	$33.33	$400.00	$1600.00	$26.67	$26.67	$400.00	$800.00	$26.67	$26.67	$400.00	$800.00
	Laboratory Supplies	<	>	<	>	<	>	<	>	<	>	<	>
	Analysis	$225.00	$100.00	$3375.00	$4800.00	$225.00	$100.00	$3375.00	$3300.00	$225.00	$100.00	$3375.00	$3000.00

[1] units are hours unless denoted by $.
= indicates equivalent cost, > or < denotes a minor lower or greater cost not tracked.
QA/QC – quality assurance/quality control

Table 11. Comparison of costs for ISM and conventional grab sampling on a per sample and total cost basis based on demonstrations at Kimama TS, Fort Eustis, and Fort Wainwright.

		Fort Wainwright				Fort Eustis				Kimama TS			
		ISM	Grab	ISM	Grab	ISM	Grab	ISM	Grab	ISM	Grab	ISM	Grab
Stage	Activity	Per Sample		Total Project		Per Sample		Total Project		Per Sample		Total Project	
Mobilization	Preparation	=	=	=	=	=	=	=	=	=	=	=	=
	Expendables	$9	$1	$129	$62	$9	$1	$129	$43	$9	$1	$129	$39
	Shipping Field Equipment	=	=	=	=	=	=	=	=	=	=	=	=
Field	Surveying/Flagging	$1	$0.92	$13	$44	$2	$1	$30	$45	$0	$2	$7	$45
	Sampling	$10	$1	$75	$31	$17	$4	$150	$60	$17	$3	$125	$38
	Decontamination	$0	$2	$0	$80	$0	$5	$0	$165	$0	$4	$0	$125
	Labeling	$2	$2	$29	$94	$1	$1	$15	$33	$1	$1	$15	$30
	Demobilization	=	=	=	=	=	=	=	=	=	=	=	=
	Shipping Samples	$25	$2	$379	$118	$8	$3	$113	$85	$22	$4	$334	$110
	Shipping Field Equipment	=	=	=	=	=	=	=	=	=	=	=	=
Laboratory	Air Drying Prep	$2	$0	$25	$0	$2	$0	$25	$0	$2	$0	$25	$0
	Sieving	$2	$0	$25	$0	$2	$0	$25	$0	$2	$0	$25	$0
	Milling	$4	$0	$63	$0	$4	$0	$62	$0	$4	$0	$63	$0
	Cleaning Milling Equipment	$8	$0	$125	$0	$8	$0	$125	$0	$8	$0	$125	$0
	Sub-Sampling	$8	$0	$125	$0	$8	$0	$125	$0	$8	$0	$125	$0
	QA/QC	$27	$33	$400	$1600	$27	$27	$400	$800	$27	$27	$400	$800
	Laboratory Supplies	<	>	<	>	<	>	<	>	<	>	<	>
	Analysis	$225	$100	$3375	$4800	$225	$100	$3375	$3300	$225	$100	$3375	$3000
Total		**$323**	**$143**	**$4763**	**$6829**	**$311**	**$141**	**$4574**	**$4531**	**$325**	**$141**	**$4,748**	**$4186**

From a statistical basis (e.g., the Central Limit Theorem), *n* incremental samples, each prepared from *k* increments, will produce data that is roughly of similar quality for the estimation of the population mean of the DU as $n \times k$ grab samples. On the basis of this simplistic theoretical model (which likely over estimates the quality of the ISM results to a degree in practice), the cost of sampling *n* ISM samples of *k* incremental in the field will be no greater than the $n \times k$ grab samples. The cost of the former would be expected to be less than that of the latter because ISM would entail the use of less sample containers, labeling, and documentation. Even if comparable field sampling costs are estimated for the grab and ISM samples, the ISM approach will result in a cost savings owing to the smaller number of laboratory analyses required.

Similarly, if each grab sample is assumed to weigh on the average 150 g and each ISM weighs 1500 g, but $n \times k$ grab samples produce the same quality of data as *n* ISM, it follows that the total weight of the grab and ISM samples that need to be shipped is $150\ g \times n \times k$ and $1500\ g \times n$, respectively. Therefore, the cost of shipping *n* ISM samples should be about one tenth the cost of shipping $n \times k$ grab samples. The cost of sample disposal would be similarly reduced.

The ISM approach will result in a cost savings for the determinative (instrumental) portion of the analytical method of a factor of *k.* However, the additional sample preparation steps needed for the ISM approach increases the total per-sample laboratory analytical cost for each metal analysis, which includes the cost of sample preparation and instrumental analysis. Additional sample preparation is required for both the environmental samples and batch QC samples such as method blanks and LCSs. Owing to the sample mass that needs to be processed (e.g., milled), the preparation of LCS for the ISM approach is more costly than that for the grab sampling approach. It is conservatively estimated that the ISM approach will increase the total per sample laboratory analysis cost by a factor of no more than two. The sample preparation procedures (e.g., which entail drying sieving and milling) are similar to those used for Method 8330B, which increased the cost of these analyses by about $150 (Hewitt et al., 2009), approximately doubling the per-sample cost of an explosive analysis. Similarly, a LCS from Environmental Research Associates (ERA) for the analysis of metals using the ISM approach is similar to that for an LCS for the analysis of the ISM method for explosives 8330B. As the per-sample cost for the analysis of a soil sample by a commercial environmental testing laboratory for TAL metals by Method 3050B/6010B is about $100, it is reasonable to conclude that the per sample cost for the ISM approach will increase by no more than a factor of two. As $k = 100$ for this effort, the total laboratory portion for the ISM laboratory analyses should be smaller than total laboratory cost for discrete sample analyses by a factor of $k/2 = 50$.

7.2 COST DRIVERS

The main cost drivers that should be considered in selecting the ISM technology for future implementation are the number of DUs or SUs sampled, the number of replicates collected, and the mass of the sample. The key site-specific characteristic that will significantly impact cost is the degree of contaminant heterogeneity expected. If an aqueous metal release occurred then contaminant heterogeneity is likely to be low and milling of the sample may not be necessary, because adequate precision can likely be achieved without this sample preparation step. However, if metal residues were released into the environment then sample heterogeneity is likely to be high and milling will be required. Milling adds approximately $100 to per sample

cost (Table 10); although the total project costs are likely to be lower depending upon the number of grab samples that would have been collected.

Sample theory indicates that cylindrical cores should be collected. The use of scoop type of samplers therefore is discouraged. A device such as CMIST, which collects a cylindrical core, is desired and the cost investment is modest and can be recouped through repetitive use of the sampler. A low cost alternative includes the use of 50cc syringes with the tip cut off that can then be pushed into the ground to collect a core and the plunger is used to eject the soil. A single syringe can be used for multiple increments from the same DU. This device works well in soft unconsolidated soils.

There should be no impact on ISM implementation based on these cost drivers. The biggest cost driver is the purchase of milling equipment by the environmental laboratory and setup of a dedicated sample processing room. At present a limited number of commercial laboratories have made the investment of milling equipment. However, as the demand for milling increases as a result of regulatory requirements, it is anticipated that more laboratories will add this to their service capability.

7.3 COST ANALYSIS

For our cost analysis we considered the need to sample a single DU utilizing triplicate ISM samples as compared to the collection of 7 or 15 conventional grab samples (Table 10). The DU consisted of a small arms range berm 100 m long by 9 m high. The sample depth was 5 cm and the standard metal TAL was assumed. We also assumed a one-time sampling event. We assumed a field sampling crew of two individuals, although for the demonstration we used either three or four individuals to speed up the sampling process.

Sample preparation costs were considered equivalent for ISM and grab samples, although it has been our experience that the same degree of planning used for ISM is not afforded to conventional grab sampling. However, our assumption was that the same degree of planning and organization of field equipment would occur for both sampling approaches. The expendables used in the demonstration are slightly different and account for a slight cost difference. In the case of grab sampling, the samples are collected in 4 oz amber glass wide mouth jars, which is the norm in environmental sampling. The ISM samples are collected in 15 x 15 inch 3 mil plastic bags and secured with a sample label and twist tie. This type of container is used to accommodate the larger volume of soil collected. It should be noted that similar sample collection containers could be used for both sampling approaches. Because the same field equipment is used, the mobilization/ shipping costs are largely equivalent.

In the field, each individual grab sample is typically surveyed because it has a unique sampling location. In contrast, with ISM the DU is the unique location so only a single corner of the DU needs to be surveyed if the DU is easily demarcated on a map or aerial photograph. If the boundaries are less clear, then each corner of the DU can be surveyed. Individual increment sample locations do not need to be surveyed. The sampling activity is essentially the same, although with ISM multiple increments are collected and combined to form a single sample. Cylindrical cores need to be collected with ISM to satisfy sample theory. In the demonstration,

both ISM and grab samples were collected with the CMIST. However, grab samples are typically collected using a metal scoop by individuals working in the environmental consulting industry.

Decontamination of the sampling tool used for ISM between increments is not needed as long as the samples are being collected from within the same DU. While this is not true of replicate samples collected from the same DU, cleaning of the sample tool between replicates is a good management practice and should help to ensure the statistical independence of the replicates.

In contrast, each grab sample is unique and thus requires either disposable sample tools or decontamination between samples. Our decontamination procedure consisted of an acetone rinse followed by a triplicate deionized water rinse. Our cost analysis does not include disposal of rinse of water. However, recovery of this waste water would add slightly to the per sample and total project costs for grab sampling. Because there are typically more samples to label using the grab approach, more time is required for this activity. Field demobilization and shipping of equipment costs are essentially equivalent as discussed earlier in regards to mobilization activities. There is a difference in sample shipping costs between the two approaches. Although fewer soil samples are collected with ISM the mass of material collected is 5 to 10 times larger than a grab sample. This more than offsets the greater number of grab samples collected.

The conventional grab sampling approach typically does not involve sample preparation. In some cases a portion of the soil may be air-dried and given a couple turns in a mortar and pestle. However, discussions with commercial environmental laboratories indicate this is not typical, unless the client specifies this activity. The typical approach is for the laboratory to open the 4 oz jar and scoop 0.5 to 2g of material off the top to be used for digestion. As discussed previously, ISM involves air-drying, sieving, milling, and sub-sampling.

Because more grab samples are collected than with ISM, the associated QA/QC costs are higher. The QA/QC analysis includes matrix spike, matrix spike duplicate, laboratory duplicates, and process blanks. This also holds true for the analysis cost, which is the same for both types of samples but more samples are collected and analyzed with the grab approach.

Our cost analysis indicates field sampling using ISM is $20-40 higher per sample than conventional grab sampling (Table 10). This is largely a function of the greater amount of time needed to collect the ISM sample, i.e., the collection of multiple increments. Similarly, laboratory preparation costs run $40-60 higher with ISM and analysis, which includes QA/QC, is double the grab sample cost. This is largely a function of ISM requiring processing of the sample, whereas conventional grab sampling typically does not involve sample preparation activities. Therefore, on a per sample basis the cost of ISM is approximately 55 to 65% higher than conventional grab sampling. The per sample cost for sampling soil with metal residues with ISM ranges from $300-$385.

However, the total project cost with ISM is lower than the conventional grab method. This is due to more samples typically collected with grab sampling. For a typical small arms range DU, three replicate ISM samples would be collected versus 7 to 15 conventional grab samples for the same DU. Therefore, total project costs are to 5 to 50% lower with ISM. The cost savings become greater as the number of DUs/SUs sampled increases. The reduction of costs with ISM is primarily a function of the fewer number of samples needed to adequately characterize an area.

8.0 IMPLEMENTATION ISSUES

Promulgation of USEPA Method 8330B (USEPA, 2006) has resulted in increased application of ISM and recognition that this approach may be applicable to other analytes in addition to energetics. ITRC (2012) recently published a guidance document that discussed in great technical detail the theory and application of ISM. The application of ISM to metals has been discussed increasingly by the DoD/U.S. Army, other government agencies, Federal and state regulators, environmental consultants, and commercial laboratories. A possible protocol for applying ISM to sites with surface soil containing metallic residues was recently published (Clausen et al., 2013b). The ISM sampling strategy is also now mandated by the states of Alaska (Alaska, 2009) and Hawaii (Hawaii, 2008) for all surface soil sampling situations and analytes. Presently, the authors of this document are working with the USEPA to modify and update SW-846 Method 3050B to accommodate ISM with the new Method referred to as Method 3050C. Proposed Method 3050C includes changes to the laboratory sample preparation procedures including milling of the samples and the addition of an Appendix discussing the application of ISM in the field. The proposed changes to Method 3050B are similar to those recommendations presented in Clausen et al. (2013b). Much of the Appendix language is similar to the additions made and promulgated in USEPA Method 8330B. The USACE Environmental and Munitions Center of Expertise and DoD are considering changes to existing guidance incorporating ISM.

The field demonstrations conducted at the three test sites indicate ISM is readily implementable (Clausen et al., 2013a). No special field equipment is required beyond what is typically used for collection of conventional grab surface soil samples. It is recommended that a sample corer device be used so that a cylindrical soil sample is collected to adhere to Gy's theory (1999, 1992). Environmental sampling performed with metal scoops should be discouraged since they don't provide a representative sample (ITRC, 2012).

The additional laboratory processing steps outlined with ISM are more involved than what has been used for conventional grab sample processing (Clausen et al., 2012b). The larger sample volume and the need for sample drying, sieving, and milling necessitates a dedicated room at the laboratory for sample processing. This may be problematic for some of the smaller commercial environmental laboratories but discussions with the larger firms indicate this is not an impediment to implementability. A number of the larger commercial environmental laboratories have such dedicated sample processing facilities.

Equipment for milling of the soil samples is a potential limiting factor to the implementability of ISM. Few commercial environmental laboratories have a Puck, Puck and Ring, or Roller/Ball Mill. Although a Puck or Puck and Ring Mill are expensive, a Roller/Ball Mill is more affordable. If one is interested in the potential cross-contamination from metallic components of the Puck or Puck and Ring Mill, agate bowls and pucks are available. However, currently available agate bowls and pucks are small, i.e., they generally hold < 600 g material, thus requiring multiple milling operations to process the entire lot of a single sample. Furthermore, agate milling equipment is expensive compared to steel. A Roller/Ball Mill with Teflon lined cans and ceramic chips is a lower cost alternative to the Puck and Puck and Ring Mills as demonstrated by Clausen et al. (2012b).

The other laboratory changes include: sub-sampling to prepare the digestion aliquot, digesting an aliquot minimum mass of 5 g, using a consistent acid to soil ratio, and addition of alternative acid solutions for some metals such as antimony and tungsten which have poor recoveries with the standard acid digestion procedure of Method 3050B. Discussions with a number of commercial environmental laboratories indicate all of these proposed changes are readily implementable but result in larger unit costs for the metal analyses.

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APPENDIX A

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